THE ONTARIO-CANADA RESEARCH COORDINATION GROUP LRTAP-ACIDIC PRECIPITATION SEMINAR

KILLARNEY, ONTARIO

SEPTEMBER 24-27, 1979

QH
541.2
.S86
1979
MOE

Copyright Provisions and Restrictions on Copying:

This Ontario Ministry of the Environment work is protected by Crown copyright (unless otherwise indicated), which is held by the Queen's Printer for Ontario. It may be reproduced for non-commercial purposes if credit is given and Crown copyright is acknowledged.

It may not be reproduced, in all or in part, part, for any commercial purpose except under a licence from the Queen's Printer for Ontario.

For information on reproducing Government of Ontario works, please contact Service Ontario Publications at copyright@ontario.ca

SUMMARY OF PROCEEDINGS OF THE ONTARIO-CANADA RESEARCH COORDINATION GROUP LRTAP-ACIDIC PRECIPITATION SEMINAR

AUTUMN MEETING

SEPTEMBER 24 - 27, 1979

KILLARNEY MOUNTAIN LODGE
KILLARNEY, ONTARIO

CO-SPONSORED BY:

Federal	Department of Environment Department of Fisheries
Provincial	Ministry of Environment Ministry of Natural Resources

Note: All data tabulations, figures, and graphs are not to be used, referenced or quoted without the written permission of the author as identified herein.

TABLE OF CONTENTS

I SEMINAR OBJECTIVES

II SUMMARY OF SESSIONS

A. SESSION 1 - Emission Inventory and Atmospheric Transport Modelling

1. Session Introduction - D. Whelpdale

2. Presentations

a) Ontario Emission Inventories - L. Shenfeld

b) Emission Inventories for North eastern U.S. and Eastern Canada - F. Vena

c) Mathematical Modelling - A. Venkatram

d) Comparison Between Measured and Computed Sulphur Compounds in Eastern North America - E. Voldner

e) Prediction of Rain Acidity and SO_2 Washout In Eastern North America - L. Barrie

3. Open Discussion

4. Session Recommendations

B. SESSION 2 - Sinks and Relative Deposition Strengths

1. Session Introduction - J.R. Kramer

2. Presentations

a) Provincial Acid Precipitation Deposition Network - M. Lusis

b) Specific Lakesite Deposition Program - W. Scheider

c) Heavy Metal Deposition - D. Jeffries

d) National Atmospheric Chemistry Network - L. Barrie

e) Great Lakes Basin - i) Cansap Network - D. Whelpdale
ii) CCIW Network - C.H. Chan

f) Alkalinity Methodology as Related to Soft-Water Measurements - S. Villard

3. Open Discussion

4. Session Recommendations

C. SESSION 3 - Susceptibility and Regime Response to Atmospheric Loading

1. Session Introduction - H. Harvey

2. Presentations

a) Effects of Acid Precipitation on Terrestrial Systems - S. Linzon

b) Lake Hydrology and Acid Loading - W. Scheider

c) Preliminary Results of Lake Susceptibility Surveys - J. Allin

d) Aquatic Setting of the Algoma Area Watershed Studies - J. Kelso

e) Chemistry of Turkey Lake Basin - F. Elder

f) Terrestrial Environment of the Algoma Watershed Study - I. Morrison

g) Lake Acidification Studies in Nova Scotia - J. Kerekes

h) Aluminum Controls - A Preliminary Model - J. Kramer

i) Alkalinity Deficiency as an Index of Acidification - M. Thompson

3. Open Discussion

4. Session Recommendations

D. SESSION 4 - Socio-Economic Aspects of the LRTAP Problem

1. Session Introduction - M. Johnson

2. Presentation

a) The Economic Implications of Acid Precipitation - J. Donnan

3. Open Discussion

4. Session Recommendations

E. SESSION 5 - Remedial Measures

1. Session Introduction - T. Brydges

2. Presentations

a) Findings from an in situ experiment using limestone to enhance the hatching success of trout eggs - J. Gunn

b) MOE Experience of Remedial Efforts in Sudbury Area - B. Keller

3. Open Discussion

4. Session Recommendations

F. SESSION 6 - Future Directions

1. Session Introduction - F. Elder

2. Presentations

a) MOE Fiscal 1980/81 LRTAP Program - E. Piche

b) Federal DOE LRTAP Program - H. Martin

c) MNR Fiscal 1980/81 LRTAP Program - J. Allin

d) Federal DFO LRTAP Program - R. Thomas

3. Open Discussion - Discussion of Future Meetings

4. Session Recommendations

III LIST OF APPENDICES

IV LIST OF PARTICIPANTS

V BUDGET SUMMARY

I SEMINAR OBJECTIVES

1. To encourage the informal exchange of current data from field programs.

2. To exchange current program information and identify weaknesses or gaps.

3. To outline for all participants the manner by which study results will ultimately be used to develop government policy, thereby, fostering and encouraging a holistic rather than a myopic view of this complex issue with the ultimate aim of maximally utilizing currently limited resources.

   For the above purposes, Mr. Piche circulated on Monday evening several documents (see Appendices One and Two) with the instructions that conference attendees were to read them carefully and submit appropriate recommendations as soon as possible regarding Appendix Two.

4. To encourage, where possible and appropriate, the involvement of regional Ministry personnel by providing an informal forum for the interchange of all relevant "non-program funded" data.

II SUMMARY OF SESSIONS

A. SESSION 1 - Emissions Inventory and Atmospheric Transport Modelling

1. Session Introduction - D. Whelpdale

a) Emissions Inventory

In the past two years, we have learned that it is more appropriate to deal with the problem of long range transport of air pollutants using a holistic approach because of the various interdisciplinary connotations involved. For example, when the bio-geochemical cycles of substances such as Nitrogen or Sulphur are discussed, the problem encompasses various separate disciplines: emissions, transport, and transformation; deposition - soils and water. Emissions inventories were first developed for control strategy purposes but the needs of modellers are different.

b) Atmospheric Transport Modelling

Models are used to describe atmospheric behaviour in mathematical terms and the relation between sources and receptors of pollution. They are important as prediction tools as well. However, models should not be considered as a panacea but as tools to be intelligently used as they will be heavily relied upon for science and policy development. Basically, there are two types of models, short term and long term, which will be discussed during this session.

It is imperative that this session achieve the collaboration between emissions inventory personnel and modellers as well as outline future modelling

needs with specific reference to the anticipated Canada - U.S. treaty discussions.

The ultimate necessity of this cohesive approach between modellers and emissions inventory personnel is dictated by the need to be able to predict the environmental signifigance of specific area sources and consequently, formulate appropriate abatement scenarios.

2. Presentations

a) Ontario Emission Inventory - L. Shenfeld

Mr. Shenfeld gave an overview of the paper, "Ontario Pollutant Inventory Information", which is included in total as Appendix Three.

The following recaps the discussion throughout and resulting from the above presentation:

LEN BARRIE: As you realize, there are hourly, diurnal, and seasonal changes in SO_2 emissions. What sort of error would you attach to your annualized average emissions?

LOU SHENFELD: For a power plant, the swing of emissions is very great. If on a particular day, verification is needed, then you have to go back to those responsible for hour-to-hour hour emissions for that day. If average emissions are what you want, then you can use the emissions inventory.

GREGG VAN VOLKENBURGH: I'm concerned that the actual operating figures and installation capacity figures may differ. Do you keep both figures on record simultaneously?

LOU SHENFELD: Yes, we do.

GREGG VAN VOLKENBURGH: Do other people give both figures; for example, in the States?

LOU SHENFELD: We have obtained emission figures from Michigan and they are normally done the same.

SERGE VILLARD: Would you say that your figures are an overall underestimate or an overall overestimate?

LOU SHENFELD: I would say our SO_2 figures are very much in the ballpark but that for particulate matter, we are underestimating. For NO_x, I cannot say. Because most NO figures are expressed as NO_x, then they may be an overestimate as the figures are for NO_2 not NO. Throughout the States, the NO_x figures are given as NO_2, but emissions are primarily NO.

EVA VOLDNER: Do you have any figures on primary sulphate?

LOU SHENFELD: No, we have not compiled any emissions of sulphur as such.

EVA VOLDNER: Are you familiar with the EPRI and SURE phase two emissions inventory where they differentiate between NO and NO_2, and SO_4 and SO_2?

LOU SHENFELD: I think only a very small percentage would be SO_4 and that would only be important in various regions. However, NO and NO_2 are important.

MARIS LUSIS: What is the status for hydrocarbons in various regions? Are they important for the oxidation of NO and/or NO_2?

LOU SHENFELD: All are based on emission factors and the accuracy is not certain. We obtained the figures early from steel companies and decided they were in error and got another set of figures.

MARIS LUSIS: Has there been a systematic attempt to get hydrocarbon data for the province?

LOU SHENFELD: Yes, there has been an attempt but the accuracy is not definite.

MARIS LUSIS: Are all hydrocarbons expressed as methane?

LOU SHENFELD: No, they vary from one plant to another.

GREGG VAN VOLKENBURGH: For NO_x and hydrocarbons, do you have estimates of natural emissions?

LOU SHENFELD: We do inventories on anthropogenic sources and the federal government, I believe, is looking after the natural sources.

EVA VOLDNER: In your particulate emissions inventory, do you do a breakdown into trace metals?

LOU SHENFELD: For lead we do, but that is the only one.

EVA VOLDNER: Do you look at particulate size and distribution?

LOU SHENFELD: No, we do not.

DOUG WHELPDALE: (Addressed to modellers in audience) Are the Ontario emissions inventories adequate for the modelling people? In other words, are the temporal and spatial variations adequate?

A. VENKATRAM: At this point in time, most models are extremely crude and the chemical and dispersion parameters are also still crude. The emissions should be within a factor of 50 percent since most models cannot really distinguish between finepoint emissions yet.

EVA VOLDNER: It would be useful to have this information. Take, for example, Ontario Hydro which has most of its emissions in December, January, and February.

LEN BARRIE: At least a seasonal variation is important.

LOU SHENFELD: In the case of Ontario Hydro, the emissions depend on how well the nuclear plant is operating and on the water resources at Niagara Falls. The fossil fuel plants were peaking plants but since they are now selling power to the U.S., the seasonal swing is not as large. In any event, seasonal and diurnal variations are recorded. For example, Lakeview might not be operating on any particular day and to predict hourly levels, we only

need to know the emissions at that time. For comparative purposes, we have the emissions inventory figures for 1978.

b) Emission Inventories for the Northeastern United States and Eastern Canada - F. Vena

Frank Vena gave a general outline of the programs in this area by Environment Canada.

The Air Pollution Control Directorate has a manmade emissions inventory of SO_2 for 1970. This inventory is to be updated biannually. The most current inventory is for 1974. The full 1976 inventory is scheduled for completion in early 1980.

Two inventory files are currently being kept: point sources and area sources. For point sources, data is collected for natural gas plants, power generating plants and smelting plants. The information on a plant by plant basis includes the location (latitudinal and longitudinal coordinates), stack parameters, annual emissions totals and where possible, seasonal variations and pollution control information.

For area sources, the emissions are relatively small when taken on an individual basis; therefore, the data is clumped together as an area source. The area which is used is county census division and the contributory sources would be residential, commercial and gas powered vehicles.

We have entered into a joint program with the U.S. Environmental Protection Agency whereby an inventory of man-made emissions of sulphur dioxide and nitrogen oxides for Eastern Canada, east of Saskatchewan, and for the U.S., east of Mississippi, is being compiled. Raw data is currently available.

For natural sources, a paper entitled "Characterization and Quantification of Natural Sources of Sulphur Compounds" is currently available to the public in draft form. (See Appendix Four for address.)

The U.S. has similar point and area source inventories, the latest of which is for 1975. There is also one available for 1977 on an aggregate basis for the industrial sector.

The EPRI and SURE studies have also apportioned their inventories for Northeastern U.S. on 80 x 80 km grids. The point source emissions are based on 1977/1978 data and the area sources are based on 1973-1977 data. Dr. Adams is also carrying out field work on natural sources in the U.S.

As future programs, Environment Canada intends to update the national inventory for anthropogenic sources of sulphur dioxide and nitrogen oxides for the base year of 1976 as well as compile an inventory for hydrocarbons. A study of natural emissions of nitrogen, sulphur, and hydrocarbons is also envisaged.

The following discussion ensued from the previous presentation which then became a

general discussion on emissions inventories:

JIM KRAMER: Do you have any figures or numbers on sulphate emissions as a large number of protons is not needed to oxidize lakes?

FRANK VENA: No, we have no information on sulphates, only as part of particulate data. The only figures are for the INCO stack where we have sulphate and metal particulate data.

JIM KRAMER: With regard to natural emissions, are you also looking at ammonia?

FRANK VENA: Natural nitrogen compounds include ammonia.

LOU SHENFELD: Were you actually able to identify it as ammonia?

FRANK VENA: The study was based on soil types and we were able to distinguish some of the compounds but an actual breakdown was not possible.

DOUG WHELPDALE: This is a good example of a study that requires input from an atmospheric chemistry point of view. We need a proper design of inventories.

JIM KRAMER: Do you differentiate between ammonia as a gas or ammonia as a particulate?

LOU SHENFELD: Sulphate figures are very small; therefore, from an atmospheric chemistry point of view, these figures including ammonia are very important.

JACK DONNAN: What about carbon dioxide? It is an important contributor. Do you have figures on natural emissions for carbon dioxide?

LOU SHENFELD: We can determine it on a global scale from the amount of combustion.

JACK DONNAN: Are your sub-categories coordinated with other organizations?

LOU SHENFELD: Yes, even on an international basis.

JACK DONNAN: Are the statistical factors for your data similar?

LOU SHENFELD: Yes, everyone is using the same emissions factors.

JACK DONNAN: How do you determine error for your emission factors?

LOU SHENFELD: We do an estimate from the total amounts of different pollutants.

FRANK VENA: We do it on a source by source basis, not a total as such.

JIM KRAMER: Can you get an estimate of confidence level?

FRANK VENA: Within 15 percent for Canada as a whole.

JIM KRAMER: In McLaren's report, I believe that the average factor is two times.

LOU SHENFELD: While averaging there is some smoothing over of data for one plant. One might be over and the other under. Therefore,

the average is good.

JIM KRAMER: How do you know for sure?

LOU SHENFELD: We don't.

KEN TRENT: The emission factor is rated as A, B, C, D, etc. depending on the averaging over of a number of plants. A number of plants with different operating characteristics have been investigated; we either used the figure as it was or looked at the plant and interpreted the figure. For SO_2 most factors are fairly high rated.

LOU SHENFELD: Sulphur dioxide is really a function of the percentage of sulphur in the ore bodies and we have good figures for that. However, I am doubtful about our NO_x figures as the same pressure was not there.

DOUG WHELPDALE: Compilers of inventories should make an effort to respond to the needs of modellers.

JIM KRAMER: When stack sampling, do you compare the measured value with a standard routine at another place?

LOU SHENFELD: We never use a standard routine. The routine depends on the ore body and the percentage of sulphur in the ore. We do not use the emissions factor approach.

JIM KRAMER: Did you ever predict a value and then actually measure it to see how close the figures were?

LOU SHENFELD: For large emissions the figures are very good. We never compiled figures by emission factor but rather on a point to point basis. For example, we looked at fuel consumption in apartment buildings at a given time. We used such an approach for SO_2 and particulate matter.

A long discussion on the confidence limits of the data ensued. D. Whelpdale said that for credibility a number representing confidence levels should be given. It appeared at the end of the discussion that an objective way to delineate confidence limits is still not practiced. It is true, however, that greatest uncertainties appear in NO_x inventories.

KEN TRENT: Wasn't a comparison between the inventory and actual stack measurements done for INCO?

DAVE BALSILLIE: Yes, Les Fitz made the calculations and the mass balance was within 5 percent on an annual basis for SO_2.

DOUG WHELPDALE: Do the modellers find the present inventory formats satisfactory? Is the format and degree of computerization of Canada and Ontario inventories suitable to the type of modelling you do?

A. VENKATRAM: The $SO_4^=$ inventory is important. The rule of thumb used for sulphates is that the sulphate production is 2 percent of the sulphur emissions. Is there any comment on this current practice of 2 percent conversion?

LOU SHENFELD: This is a good figure for power plants. The control amount is expressed as SO_2 not $SO_4^=$.

A. VENKATRAM: The sulphate is coming from somewhere. Therefore, we use the step conversion rate.

EVA VOLDNER: The use of scrubbers can remove some SO_2 and possibly change the conversion factor. There is a higher formation of sulphate deposition on ash particles which can constitute 10 percent or more of the total emissions.

DOUG WHELPDALE: Are the modellers using Canada or Ontario inventories in their models?

EVA VOLDNER: We are using information from Frank Vena's inventory and from Ontario Hydro.

DOUG WHELPDALE: Are they in a suitable format?

EVA VOLDNER: The Environmental Protection Service's were not previously but computerization has helped now.

A. VENKATRAM: Area sources, point sources, plus stack height are needed as well as emissions of NO_x and SO_2. The major omission is sulphates.

EVA VOLDNER: I am concerned that there is more acid in power plants.

LOU SHENFELD: The 2 percent conversion rate is not bad but 10 percent with scrubbers appears high. There would not be any value in scrubbing if there is more $H_2SO_4^=$ with scrubbers.

LEN BARRIE: A lot of plume studies have been done and the figures range from 1 percent to 5 percent of the total emissions in the MAP3S study for electrostatic precipitators.

LOU SHENFELD: Even for wet slurries?

JIM KRAMER: Proton emissions is the information that we're after.

A. VENKATRAM: How do we measure proton emissions?

JIM KRAMER: You can measure them by titrating material and measuring what is available. $SO_4^=$ is not enough. More direct work is needed. We have to wipe out a lot of assumptions as regards the exact amount of SO_2, $H_2SO_4^=$ etc.

WALTER CHAN: About one year ago, I was at a conference in the U.S. and during a discussion on primary sulphate emissions, the conversion rate of $SO_4^=$ to SO_2 was 1.8 percent. Our own measurements in the INCO stack gave a conversion rate of 1.8 percent. The Falconbridge rate was even lower. Therefore, your 10 percent conversion rate seems very high.

LEN BARRIE: The reason for the 10 percent is that modellers use a grid system and 10 percent of the area of the grid.

A. VENKATRAM: We have to get together with the inventory people to ensure that the grids for emissions and winds are compatible.

EVA VOLDNER: There is too much selection. We need user oriented inventories.

A. VENKATRAM: It is too much work lumping the emissions together.

MARIS LUSIS: There are in-stack measurement methods for proton quantification. Downwind reactions can change the picture completely due to interaction with other particulate matter. In-plume measurements relatively close to the stack are perhaps important and more relevant.

JIM KRAMER: Proton measurements are not difficult.

MARIS LUSIS: Do you trap them on teflon?

JIM KRAMER: Measurements are made in mist, and then we titrate them back. One ml of mist is needed using the gran titration method. You could also impinge them into a liquid medium and the protons should enter the solution immediately.

LEN BARRIE: Photometric detectors can also be used for measuring protons.

DOUG WHELPDALE: Is a 50 percent margin of error accurate for emissions data?

A. VENKATRAM: When we receive more resolved information, we send it back.

WALTER CHAN: What is the relative accuracy of area and point sources of NO_x?

LOU SHENFELD: When the figures are compiled from various individual countries, no comparisons can be made because the populations and

approaches taken are very different. The Canadian figure is a lot higher since the country is larger and the people drive more.

FRANK VENA: On a national basis, 60 percent of the NO_x emissions is due to automobiles. The emissions depend on various factors and as a result we cannot obtain exact statistics.

MARIS LUSIS: Could you elaborate on the hydrocarbon measurements made by the DOE?

FRANK VENA: We have had an inventory on hydrocarbons since 1970 but currently we do not have the expertise to update it.

MARIS LUSIS: To establish the role of nitrous acid on acidic precipitation requires knowledge of the chemistry of hydrocarbons, or at least of the crude breakdown of methane and non-methane hydrocarbons.

DOUG WHELPDALE: Do you have the same resolution for hydrocarbons as for NO_x and SO_2?

MARIS LUSIS: At least a seasonal resolution would be required. The photochemical processes are certainly important.

LOU SHENFELD: The emission factor approach for the normal automobile is based on methane and non-methane emissions and their reactivity. The U.S. is currently compiling inventories on hydrocarbons for control purposes. This information is not yet in data bases. Also, ozone information is needed to determine standards.

MARIS LUSIS: Are there no figures on national emissions?

LOU SHENFELD: No, only on a regional basis.

HANS MARTIN: Was the development of the SO_2 inventory for Ontario done independently?

LOU SHENFELD: Yes, we provided the federal government with our figures.

JIM KRAMER: Were they the same classification, and did they have the same emissions factors?

LOU SHENFELD: Yes.

FRANK VENA: Yes.

EVA VOLDNER: Regarding the emissions inventory projection, when will the estimates be ready with complete distribution from sources?

FRANK VENA: Both SO_2 and nitrogen oxide inventories are available now and the draft for the copper/nickel smelting production is also ready now.

DOUG WHELPDALE: What other needs do the modellers have to serve as guidance for those compiling inventories?

LEN BARRIE: There is a problem with temporal variations and we need seasonal variations.

FRANK VENA: That is one of the areas we would like to see improved.

LOU SHENFELD: We do have data on day to day variations as well as for the hour of the day. We can give a total figure as an average or a different figure for each hour depending on the season and the day.

GREGG VAN VOLKENBURGH: The nitrogen inventory could be improved and the natural emissions should be factored into the inventories. As regards the hydrocarbon inventories, the modellers should comment on when the model will be ready and the type of information needed, i.e. methane and non-methane.

A. VENKATRAM: It depends on the type of model. The Lagrangian model only yields linear equations and the Eulerian models are more complex chemically and, therefore, use too much computer space.

EVA VOLDNER: We can only use the latter on a small scale.

GREGG VAN VOLKENBURGH: Can you give the inventory people some guidance on a 3-5 year time scale?

LOU SHENFELD: Do you have any emissions data on NO_x spread by fertilizers?

FRANK VENA: No, we haven't.

GREGG VAN VOLKENBURGH: This information is important for ammonia data.

LOU SHENFELD: In Simcoe, Ontario, recently the NO_2 data went up considerably. It was later discovered that the park land around the monitoring station had just been fertilized.

WALTER CHAN: The emissions inventory on hydrocarbon is very important; even a lump sum for emissions of methane and non-methane would be useful. The Brookhaven National Laboratory may have a chemical package including the chemistry for Sulphur and Nitrogen.

LOU SHENFELD: What is the importance of hydrocarbons within the plume? Does it affect the conversion rates for $SO_2 \rightarrow HSO_4^{=}$?

MARIS LUSIS: We need more detailed chemical modelling with at least some distinction between methane and non-methane and even perhaps between oliphatics and aromatics, etc.

c) Mathematical Modelling - A. Venkatram

A. Venkatram submitted a substantial portion of his presentation and this material is included as Appendix Five.

Currently, there are two models being developed at the Ministry of the Environment, one covers the northeastern United States and the other eastern Canada.

In the statistical approach to long range transport modelling, two principal components exist. The first is the scavenging model or stochastic model and the second is the incorporation of the scavenging processes into a dispersion model. The results of this model, as regards long term SO_2 concentrations in the Sudbury area, are fairly high local concentrations. However, since the parcel moves, sulphate concentration is very widespread; Sudbury and Pennsylvania contribute a substantial amount.

At this point in the presentation, Mr. Serge Villard asked the following question: "Are both primary and secondary production included in your model?" Mr. Venkatram replied in the affirmative.

The advantage of models is that individual sources can be switched on and off. The following questions were submitted at this point:

CAL WARDEN: For a long-range, long term model, how many years of emissions data do you need?

A. VENKATRAM: Possibly 50 years back data.

LEN BARRIE: How far back does your emissions data currently go?

A. VENKATRAM: 1975.

Further results from the MOE models are the predictions of pH in the U.S. and Canada whereby a low pH area is predicted in Pennsylvania and near Sudbury.

Furthermore, model results indicate that American sources contribute 85 percent of sulphate concentration to the Sudbury area (in the very local Sudbury area, Sudbury's concentration increases to 35 percent) and Ontario contributes 45 percent to Quebec's sulphate concentration.

The following discussion resulted from A. Venkatram's presentation:

DAVID BALSILLIE: I do not agree that the model actually shows what is happening.

JIM KRAMER: Have you done any sensitivity analyses?

A. VENKATRAM: Yes, we have done them. We are also continuing work in this area. Our confidence is high as far as relative order of magnitudes are concerned. If we increase conversion rates, our sensitivity goes up 1 - 2 percent.

JIM KRAMER: Before any accuracy can be achieved, we need to parameterize the results.

A. VENKATRAM: Some meaning can be derived from the conversion rate increases.

LOU SHENFELD: Do Batelle emissions include Ontario sources?

A. VENKATRAM: Yes, but not Quebec's.

LOU SHENFELD: For Quebec, the bulge should be at Noranda. But, if a percentage is caused by Ontario in Quebec rather than from Quebec's own sources, this assumption might not be true.

There was some discussion at this point as to the relative contributions of SO_2 and sulphate to form sulphuric acid as well as the relative effects of American vs. Sudbury sources.

LOU SHENFELD: Why were NO_x's omitted in this model?

A. VENKATRAM: The Lagrangian model cannot deal with NO_x. For your information, we are currently developing a Monte Carlo approach to

modelling for monthly concentrations. If we put all this information on a grid system, then when the amount leaving is less than the amount entering, the difference is accounted for by scavenging.

MARIS LUSIS: Since the short-term model is too complex but can be validated by data and the long-term model is relatively simple but we have an inadequate data base, then is the deposition monitoring program we are currently undertaking of any value?

A. VENKATRAM: Yes, for the future.

LOU SHENFELD: We will have precipitation data plus sulphate data in the long term to verify the model eventually.

MARIS LUSIS: We are looking at a 5-year time frame and that is too short.

A. VENKATRAM: However, our validation is therefore as good as any other.

P. K. MISRA: Have you done an estimate of the averaging time on the data used in the model?

A. VENKATRAM: No, we have not.

JIM KRAMER: You can verify old sulphate data by comparison with the Greenland Icesheet data.

LEN BARRIE: Are the Ontario hi-vol samples regionally representative of background concentrations?

A. VENKATRAM: I think the numbers are in the ballpark. However, we still do not know how to validate models and the current validations are not properly done.

d) Comparison Between Measured and Computed Sulphur Compounds in Eastern North America - E. Voldner

For specific details of E. Voldner's presentation, refer to Appendix Six.

After E. Voldner stated that the ratio between computed and measured monthly $SO_4^=$ concentrations was within 60 percent of the measured value, the following inquiries were made:

JIM KRAMER: Which concentrations, the modelled or measured?

EVA VOLDNER: The modelled. We are now encouraging a 50 km radius for the grids as the monthly measurements for sulphate vary by 20-30 percent.

MARIS LUSIS: Did you use 1970 emissions data and compare the results with the measured 1977 data?

EVA VOLDNER: Yes, however, the 1977 data has only currently become available.

MARIS LUSIS: How much change was there?

EVA VOLDNER: The change is 30 percent. The inventory data has been scaled down by 25 percent since 1970. However, the emissions could still be higher for Pennsylvania and area.

LOU SHENFELD: Does it show what the variation of monthly sulphates are from one station to the next?

EVA VOLDNER: For which month?

LOU SHENFELD: October, or whatever month is best for the model.

EVA VOLDNER: It depends on the network. For the SURE network, the variation is by 1/3 in Central Ohio. Ontario Hydro, however, has different time intervals.

LOU SHENFELD: How much variance exists in the actual figures when trying to predict from station to station?

EVA VOLDNER: Not much in central areas but by a factor of three in the outlying areas.

A. VENKATRAM: Do you have any objective correlation on data?

EVA VOLDNER: Yes, there is correlation between daily averages and cross-correlation between stations and the model. The correlation coefficient varies from 0.5 to 0.8. We expect the model to vary between 0.4 and 0.9.

At this point, E. Voldner continued her presentation with a description of the MAP3S stations and CANSAP networks (Appendix Six). At the end of this presentation, the following inquiries were made:

A. VENKATRAM: Using the ratio test to evaluate models is dangerous as the numbers vary from 5 to 10 and the model predictions are equal to approximately 10.

E. VOLDNER: We will look at deposition and concentration patterns next time.

WALTER CHAN: When you compare actual sulphate concentrations with computed values, you could have artifact sulphate formation on glass fibre.

EVA VOLDNER: No comment.

JIM KRAMER: Did you do any sensitivity analyses?

EVA VOLDNER: Yes, sensitivity to scavenging was in evidence.

LEN BARRIE: For EPRI data, proper teflon coated material was used (quartzite).

MURRAY JOHNSON: What assumptions were made regarding non-anthropogenic sources?

EVA VOLDNER: No natural sources were included.

DOUG WHELPDALE: In Eastern North America, natural sources are less than 5 percent of anthropogenic.

EVA VOLDNER: In Southern Tennessee, the marshes are a significant natural source.

JIM KRAMER: I think we should look at the long range transport of natural sources.

e) Prediction of Rain Acidity and SO_2 Washout in Eastern North America - L. Barrie

For L. Barrie's presentation in detail, refer to Appendix Seven. The following inquiries and discussion resulted from the above presentation:

A. VENKATRAM: How do you incorporate the variation washout ratio into a Lagrangian model?

LEN BARRIE: There is a method outlined in the paper. (See Appendix Seven).

WALTER CHAN: There is a high correlation between H^+ to $SO_4^=$ and H^+ to $NO_3^=$ but you have not included $NO_3^=$.

LEN BARRIE: We have neglected $NO_3^=$ deliberately as modelling N cycle is difficult presently. Because intercepts in the empirical formula between H^+ and $SO_4^=$ was small, we thus neglected $NO_3^=$.

WALTER CHAN: I am surprised at a low intercept if $NO_3^=$ contribution is significant?

LEN BARRIE: If $NO_3^=$ and $SO_4^=$ were correlated there would be a significant intercept.

JIM KRAMER: Have you considered $CaSO_4$ in correlating $SO_4^=$ to H^+?

LEN BARRIE: No, we have not looked into it. $SO_3^=$ does not exist in atmospheric chemistry because it is so hygroscopic; the air takes up H_2O vapour and an aqueous drop of H_2SO_4 forms.

HAROLD HARVEY: Is the propensity to form acid rain the same for local sources as it is for long-range transport sources?

LEN BARRIE: It depends on the difference in acidity of the particulate matter. The particulate matter would be more acidic close to the source as neutralization has more chance to occur away from the source.

HAROLD HARVEY: In Algonquin Park area, the isopleths show ½ Canadian contribution and ½ American. Who is causing rain to be acidic?

LEN BARRIE: It would depend on the form--$SO_3^=$, SO_2, particulate or aqueous $SO_4^=$.

LOU SHENFELD: The scavenging of $SO_4^=$ is better than SO_2 and this would make a difference in net wet deposition.

LEN BARRIE: The fraction of total Sulphur in rain depends on particulate acidity and temperature. Particulate acidity determines the pH which determines the washout ratio for SO_2. When dissolved SO_2 hits lakes or calcareous material, it oxidizes to $SO_4^=$ which is a volatile species. Particulate sulphate concentrations in air can vary from 1-10 $\mu g/m^3$.

LOU SHENFELD: The rain is already acidic due to the acidic particulate matter and, therefore, it would not be an efficient scrubber of SO_2.

LEN BARRIE: If the ratio of particulate matter in rainwater is low, then the pH is high, and the SO_2 washout process would proceed very quickly. However, we still would predict that SO_2 washout capabilities are substantial in the fall.

LOU SHENFELD: We have measured and found no substantial difference in SO_2 concentrations when it is raining and when it is not raining because rain is a poor scavenger of SO_2. Sulphate concentrations, on the other hand, drop during a prolonged rainfall.

LEN BARRIE: The ratio of SO_2 to $SO_4^{=}$ is important. In the MAP3S measurements, out of the fraction of total S less than 1 percent is SO_2. These values increase up to 30 percent. In Canada, lower temperature would cause less acidic particulates and, therefore, more SO_2 scavenging.

DOUG WHELPDALE: Up to 1/3 could be in the form of dissolved SO_2.

DAVE BALSILLIE: In a study in 1972 carried out at Laurentian University in Sudbury, the highest levels of total sulphur occurred in rainwater before freezeup.

JIM KRAMER: Using our measurement methods, we never see the real effects of dissolved SO_2. In the molecular form, it is transferred across the biotic membrane. As aquatic SO_2 it constitutes an important link across the biotic membrane.

DEAN JEFFRIES: What is the correlation of H^+ and $SO_4^{=}$ in the CANSAP samples?

LEN BARRIE: These samples are collected for evaporation purposes.

DEAN JEFFRIES: What is the collection efficiency of the samplers?

LEN BARRIE: Close to 100 percent.

FLOYD ELDER: Have you tried it on any event data?

LEN BARRIE: No.

3. Open Discussion

D. Whelpdale, the session chairman, raised several points for open discussion.

POINT #1: Currently, we have short-term data for our long-term models. Should we continue to develop statistical models or start concentrating our efforts on episodal models?

LOU SHENFELD: Short-term data after a long period of time will be useful for our statistical models.

GREGG VAN VOLKENBURGH: From a policy point of view, aren't episode models more useful?

A. VENKATRAM: The situation is not hopeless. Episode models to date have not met the objective criterion of validation because they are complex models and comparison with actual measurements is not a trivial task. I feel that a log correlation between H^+ and $SO_4^=$ is more appropriate than a linear one. Also, I don't think that ratio tests are appropriate.

LOU SHENFELD: I corroborate A. Venkatram's comments on ratio tests.

JIM KRAMER: I don't think that H^+ is log-normally distributed. I think that there's a chemical correlation.

LOU SHENFELD: In the variance of data for monthly averages, we found that sulphates are very constant and that there was a similar average for the monthly period at all stations.

LEN BARRIE: Did the computed to measured ratio show that?

LOU SHENFELD: The predictions can range from half to twice as much and we can still have a good ratio if all the values are the same.

LEN BARRIE: The ratio test is very misleading. It is necessary to lognormally transform the data in order to reduce stochastic variance.

JIM KRAMER: That is not true for H^+; all distribution will tail off at the high concentration end.

WALTER CHAN: We have observed lognormal H^+ distribution in our Sudbury network.

MARIS LUSIS: Do you have any comments on this, Bob (Vet)?

BOB VET: The variance, both spatial and temporal for the episodal model is monstrous as compared to the statistical model and the computed data itself is highly variable too.

LOU SHENFELD: To obtain an episodal model and validate it is too difficult.

DOUG WHELPDALE: When we are only dealing with long-term effects.

LOU SHENFELD: What about the seasonal effect of short-term spring high acid run-off?

JIM KRAMER: In order to predict the acute effects on fish or marketable crops, we could use the episodal models. The data available is

as good as the model's ability to predict it. Jacobsen at Brookhaven has a slide of effects on marketable crops and he is plotting H^+ vs. time.

A. VENKATRAM: This approach has been used on short-term concentrations. I don't think that we should have to choose between the two types of models. Predicting the parameters of distribution functions would enable us to predict concentration. I feel that episodal models should also be developed.

POINT #2: Is the space-time resolution adequate in our existing models, (i.e. the direction of the Sudbury plume), for assigning the damage of acid rain in a particular area to a specific source?

GREGG VAN VOLKENBURGH: This would imply dropping the Lagrangian models and pursuing the development of the Eulerian, right?

A. VENKATRAM: Lagrangian models can also be used to obtain better resolution. They are only limited by the resolution of the data that has been measured.

P. K. MISRA: Any resolution in any model, except the box model, is limited by the wind data available. We have the same problem, the limitation of the input data. What about the resolution of the precipitation data? Scavenging depends on the precipitation rate and it is difficult to derive the precipitation rate from the precipitation amount.

A. VENKATRAM: That is an important point.

LOU SHENFELD: Can we derive answers to policy questions from Venki's model?

EVA VOLDNER: Several models are currently available at several institutions. We modellers should all get together for cross-consultation regarding the available models to limit redundancy.

DOUG WHELPDALE: What about the limitation of input data?

A. VENKATRAM: One limitation is the precipitation rate.

LOU SHENFELD: How much resolution do you want?

A. VENKATRAM: For randomly distributed rain.

EVA VOLDNER: We have objectively analyzed the precipitation data available from the Canadian Meteorological Centre. We are also acquiring network data from the States and Canada for comparison purposes. Canadian data is currently done by 24 hour events but there is pressure to go to six hour events. Jack Shannon perceived no difference in his model, though, between using one hourly or six hourly precipitation data for his averages. PNL also observed little difference between one hourly or six hourly data for averages, but for monthly data there was a great difference.

DOUG WHELPDALE: Is it possible to have the Meteorological Service produce hourly precipitation data?

GORD McBEAN: Yes, we certainly can. The hourly rates can be determined by visual estimates--light, moderate, heavy rain.

LOU SHENFELD: Are the rain gauges closed when it is not raining?

GORD McBEAN: No.

EVA VOLDNER: The rate of precipitation is not the only data limitation. We only have a few networks to monitor snowfall in the wintertime.

LOU SHENFELD: For analyzing components in snowfall, we would need an entirely different set of stations.

EVA VOLDNER: There is a host of problems involved. For comparison purposes, objectivity is almost impossible.

LEN BARRIE: In Sweden, researchers discovered that the greatest variance in regional deposition is due to the precipitation amount and to the variance in the concentration of constituents. Therefore, we need a denser network of precipitation gauges than collectors.

DOUG WHELPDALE: Which we have.

FLOYD ELDER: We are getting bogged down here. The users could not use some of this data even if we had it. Seasonal distribution is necessary and episodal distribution in small areas is also important. Large-scale space-time resolution should not be neglected for small-scale space-time resolution.

DOUG WHELPDALE: Small-scale resolution is important for certain small areas such as Muskoka-Haliburton and Algoma.

LEN BARRIE: Temporal variations are also necessary. We currently have no emissions inventory on a seasonal basis and this limits our models.

FLOYD ELDER: Extreme details are not feasible at this time since the models we currently have are not able to cope with fine detail yet.

DOUG WHELPDALE: Are we satisfied with our present modelling program?

FLOYD ELDER: I think we should make the best use of what is currently available in terms of more refinements.

DOUG WHELPDALE: With the AES modelling we hope to determine the fluxes between Canada and the U.S. and between adjacent provinces.

We should have the fluxes for sulphur at the end of this year. However, it is not adequate. We need to know the deposition in the Muskoka Lake area as well as the responsible sources. To achieve this goal, we need increased sensitivity in our model.

LEN BARRIE: Fluxes will not help. We need data on deposits and direction.

JIM KRAMER: Perhaps we should talk about a range of values for conversion rates and deposition rates rather than in absolute terms. I feel that a range of accepted values

is a better way to deal with the question of individual contributors. At the same time, we can continue to play with numbers and models.

A. VENKATRAM: Predictions from long-term concentration and variance from measured data can give us the necessary information.

POINT #3: There must be a better way to validate models than continuing to compare data. Any suggestions?

A. VENKATRAM: The assumption of linear relations between predicted and measured data is very misleading. One solution is log transformation of the data. Validation becomes difficult because data may be at one point of the distribution which models cannot predict. What is actually predicted is the mean.

LOU SHENFELD: We are limiting ourselves to the sulphur cycle and ignoring the nitrogen cycle and its contribution to acidity. There is a high degree of correlation between sulphates and H^+ but the assumption that nitrates increase with sulphates could be erroneous. In a publication by Frantisak and Hunt, it was concluded that a high concentration of nitrates in Quebec is contributing to the acidity there.

Discussion on model validation ensued. It was concluded that it was not possible to compare model outputs to real data as models predict an ensemble average whereas measured data is not an ensemble average.

A. VENKATRAM: Model validation is not what is necessary but model calibration is.

At this point, the session chairman, Doug Whelpdale, asked for the program managers' viewpoints on this issue.

ED PICHE: If a consensus on interpretation is what is needed, then we need more time not money. Otherwise, the result of modelling will surely be a spectrum of disagreement.

FLOYD ELDER: Regarding validation of models, I think it is possible to validate them on scales that do exist. However, it is difficult to integrate different data, such as temporal and spatial variations in deposition, into a model.

On the one hand, management is tempted to believe in models; on the other hand, it should use models intelligently, i.e. to devise several scenarios with them. In addition, models can be used to test sensitivity to various parameters. For example, H^+ data may not be the data needed by the modellers; they may need different data to verify models.

DOUG WHELPDALE: We must carefully analyse the model's output. Accuracy limits and qualifying statements should accompany a model.

HANS MARTIN: We have assessed various aspects of the L.R.T.A.P. problem and recently modelling has assumed a new significance. The reasons are: 1) they can be used to develop scenarios for the future and 2) we cannot wait for adequate field data because

of pressure from the U.S. which has similar feelings regarding models. Therefore, we have to deal with models.

GORD McBEAN: Modelling is in the stage now that weather forecasting was in about 30 years ago. We should take advantage of these 30 years of meteorological techniques for validation of models, gridpoints, and resolution. Also, I think it is essential that modelling progress to shorter time and space scales.

FLOYD ELDER: Is computer time limiting us from reducing our grids to 100 km?

GORD McBEAN: 380 km. is the standard CMC grid size because it is the typical mean spacing between upper areas. For limited area, fine mesh models, we use 127 km. grids and 63 km. grids.

LOU SHENFELD: If variance is not large at the upper levels of the atmosphere, it does not necessarily mean that the accuracy is poor.

A. VENKATRAM: We lose predictability at the boundary layer because processes are more complex there.

4. Session Recommendations

a) Emissions Inventory

1. To broaden the scope of inventories to include the following emittants:

- NO_x
- sulphate particulates

- ozone
- hydrocarbons both methane and non-methane groups
- natural emissions of sulphur and nitrogen
- total suspended particulate emissions broken down into constituent elements

NOTE: In all cases, including SO_2 inventories, all appropriate emission source characteristics should be recorded, in particular stack height, stack diameter, exit velocity.

2. To assign estimates of uncertainty or error to all emissions inventories and in addition, include information pertaining to diurnal and seasonal variations, if any.

3. To ensure the accessibility of all inventories to the users thereof and in addition, ensure that the format reflects the needs of the modelling community.

4. To include atmospheric chemists in all deliberations related to establishing inventory requirements and formats.

b) Atmospheric Transport Modelling

1. Appoint a Federal/Provincial/International Committee of modellers.

2. Instruct this committee to put on paper well-defined objectives, tasks, and associated timeframes.

3. Instruct this committee to prepare as soon as possible a review paper on the state-of-the-art of modelling and appoint an appropriate spokesman to brief senior management on at least an annual basis for the next five years.

4. Put priority on improving our understanding of the chemistry of nitrogen oxides.

B. SESSION 2 - Sinks and Relative Deposition Strengths

1. Session Introduction - J. Kramer

To begin with, J. Kramer emphasized that the terms pH and total hydrogen ion concentration are not synonymous. He then reviewed several of the contemporary methods for measuring alkalinity.

Alkalinity analyses and the Gran approach--some observations

Low level alkalinity measurements are now being carried out using the Gran analysis. This procedure is to be desired and if automated gives good results. Some precautions are required however.

1) The analysis to be precise must be carried out in a medium of constant ionic strength which is constantly being stirred. Suggested ionic strength for soft waters is 0.01 NaCl or KCl.

2) The electrode system must be linear in the titration range which can be ascertained by titrating an acid or base with a blank NaCl or KCl solution and regressing, log (v/V+v) vs. pH' or E, where v, V, pH', and E are respectively, titrant volume, sample volume, apparent pH and milli-voltage.

3) The titrant volume to sample volume must be very small typically less than 1%.

4) The Gran dilution function $[H]$ (V+v) is only valid when $[H]$ is much greater than any protolyte. Therefore, it is invalid at the

equivalence point and becomes progressively more valid at lower pH. When the [H] is about 10X that of the equivalence point (one pH unit), there is a 1% 'error' typically. A computer system can correct for this effect by an iterative calculation.

5) With the level of precision obtainable, temperature effects can be important.

In conclusion, he stated that several relevant issues for this session were similar to issues in the first session. e.g. spatial distance and time intervals.

2. Presentations

a) Provincial Acid Precipitation Deposition Network - M. Lusis

Sudbury Environmental Study's Precipitation Network

Objective: To measure the impact of the smelting operation on precipitation chemistry and loading in the Sudbury area.

Methodology: 1) Monthly sampling for loading estimates.

This monthly wet-only sampling using Sangamos started last fall. Rain gauges were also set up. The samples are analyzed for pH, acidity, major ions and dissolved trace metals.

2) Event sampling for directional source identification.

Event samplers are used to determine the frequency and intensity of precipitation. 24-hour bulk collectors are used and the sampling parameters are pH, acidity, major ions, and dissolved trace metals. The number of samplers varies with the time of year. Twenty samplers are used in the summer while there are only ten for the winter. The actual collection is carried out by volunteers. This study will end in May 1980.

Nanticoke Environmental Management Program
Precipitation Network

Objective: To measure the impact of the Nanticoke industry on precipitation chemistry and loading in the Nanticoke area.

Methodology: Monthly sampling using Sangamos and rain gauges. There are currently six collectors and the network is expected to continue for several years. The samples are also analyzed for pH, acidity, major ions, and dissolved trace metals.

APIOS/Atmospheric Research

ARB Objectives:

1) To determine the wet and dry deposition fields of acids and related constituents in Ontario

and the frequency and intensity of acidic precipitation episodes.

2) To determine, through meteorological analysis and mathematical modelling, the contribution of Ontario and non-Ontario sources to the phenomenon of acid precipitation.

3) To determine the present condition and eliminate possible trends in soil quality caused by acidic precipitation on vegetation.

Precipitation Measurements for APIOS

1) Cumulative Network: To determine the wet deposition fields across the province.

The methodology currently under consideration is the use of Sangamo samplers with monthly collection since currently there is no hard evidence that monthly collections are worse than event or weekly, except perhaps in the case of sampling nutrients. The samples are analyzed for pH, acidity, conductivity, major ions ($SO_4^{=}$, $NO_3^{=}$, Cl, NH_4, K, Ca, Mg, Na), dissolved trace metals (Cu, Ni, Zn, Pb, V, Cd, Fe, Mn, Al), and nutrients (Total P, TKN).

As regards the actual selection of sites for the monthly deposition monitors, we are currently considering the deposition fields determined by CANSAP and A. Venkatram's models. The sites should be non-urban and away from strong sources. The distribution of the samplers should allow us to obtain deposition isopleths. Sites should meet the criteria for regional scale monitoring of precipitation chemistry.

It was noted at this time that APIOS' Sangamo sampler design was different from CANSAP's. Bag inserts are used for both the wet and dry side samples; then the sample bag is heat sealed in order to make the sending of the monthly sample in a bag feasible.

2) Event Networks: To determine the frequency and intensity of acidic precipitation episodes; to identify the direction and source; to validate mathematical modelling.

Currently the collector design is being evaluated by contract. We should have the results on the wet deposition monitors by Christmas (1979) and then we will purchase our snow collectors.

The samples from the event network are analyzed for pH, acidity, conductivity, major ions. Particulate measurements will also be made ($SO_4^{=}$, $NO_3^{=}$, $HNO_3^{=}$, SO_2).

Current plans call for 24 hour sampling at three sites. Tentatively, these event cluster sites are set for:

a) London, Ontario - in order to obtain direct information on loading with the States and Northern Ontario and also to assist in trajectory analyses.

b) Quebec - Ontario border - in order to obtain information of Ontario's emissions into Quebec.

c) Dorset area - in order to assist the WRB with its studies of the area.

Dry Deposition Measurement

Objective: To determine dry deposition fields of gaseous and particulate sulphur (as well as some of the other particulate constituents) on a seasonal basis.

Methodology: 1) SO_2:

Dry deposition rate = deposition velocity X concentration

For the deposition velocity, we need to extend the Argonne deposition velocity work through Ontario to obtain seasonal maps of deposition velocity across the province. For concentration, we use a passive SO_2 sampler. An impregnated filter is set behind a permeable membrane (Nucleopore) that traps SO_2. A one month long experiment indicated that the average is roughly proportional to the mass collected on the filter paper. We presently have a contract out to evaluate this method in the laboratory and in the field. The problem is that the deposition is not constant but would depend on windspeed. However, we could still arrive at seasonal average deposition rates.

DAVE BALSILLIE: How dense a dry deposition network are you planning?

MARIS LUSIS: We plan to place passive samplers at the Sangamo sites.

2) Particulates: There are two methods to measure particulates:

a) dry deposition rate = deposition velocity X concentration $\{SO_4^{=}\}$

The deposition velocity is again obtained by an extension of the Argonne map and the concentrations are obtained using the provincial hi-vol network.

b) Use Sangamo dry side buckets.

Related Projects to APIOS

1) Intercomparison of APIOS/CANSAP and APIOS/CCIW samplers and results at 10 stations.

2) Snow simulation studies for snow simulation gauges (U. of T.).

3) Event precipitation sampler evaluation (UTS).

4) Passive sampler evaluation (UTS).

5) Sample handling and analysis experiments (LSB).

6) Development of a meteorological data acquisition system for quickly determining air mass origins associated with acidic precipitation events (real-time accessing); storage of surface and upper air meteorological data; computation of trajectories, using these data, (on IBM 370).

7) The APIOS Chemistry Data Base (Ph. D. associates Ltd.).

After Maris Lusis outlined a tentative schedule of events for completion of aspects of the study (see **Appendix** Eight), the following discussion occurred.

HANS MARTIN: For your deposition velocities, have you taken diurnal and seasonal variations into account?

MARIS LUSIS: To obtain seasonal estimates across the province, we plan to use the method used by Hicks' group at Argonne.

GREGG VAN VOLKENBURGH: Why is the NAPD network doing weekly collections and CANSAP and APIOS doing monthly?

DOUG WHELPDALE: That was a compromise because NAPD could not afford sampling on an event basis but did not want to carry out sampling on a monthly basis because they feared sample degradation.

MARIS LUSIS: There is no hard evidence to show the difference between the two. We analyzed SES data and it was difficult to see the difference between event and monthly sampling.

JIM KRAMER: Why not sample every two weeks?

GREGG VAN VOLKENBURGH: Then you have a problem concerning comparability.

DOUG WHELPDALE: Data input is as collected and the format is taken as may be desired. However, four weeks do not add up to a month.

LOU SHENFELD: There would also be the problem that there is no comparable data for those samples.

NELS CONROY: Dry deposition for SES was based on dry deposition velocities. However, the estimates of dry deposition velocities of hi-vols are still due.

MARIS LUSIS: Until Argonne's map is extended into Ontario, estimates could be made from the hi-vol network. The validity of extending Argonne's work by stratifying SES samples is questionable since we have no real seasonal average.

NELS CONROY: We need more of a field season.

MARIS LUSIS: Until then, we continue to make estimates.

b) Specific Lakesite Deposition Program - W. Scheider

For more detailed information on this presentation, please refer to Appendix Nine.

The focus of our work is lake oriented and we are primarily interested in the effects of environmental stresses on the chemistry and biology of the lakes. However, in the pursuit of this knowledge, we stray into other areas such as precipitation inputs and watershed inputs.

Our precipitation networks are centred on study lakes in the Dorset and Sudbury areas. I will discuss the input of ions in precipitation at Dorset.

At sites in Dorset, we have two kinds of collectors, one bulk and one wet only. The bulk collector is a ¼ m^2 stainless steel, teflon coated funnel and it is continuously open. The wet only collector is triggered to open during the precipitation event. Also, at the sites we have a 10 cm. diameter rain operation since the summer of 1976 and the ion deposition data has been worked up to the fall of 1978. We collect our samples at variable intervals when enough precipitation has fallen to do the full range of analyses to generate monthly deposition.

Mean Annual Concentration Data
August 1977-1978

Bulk µeq/l				Wet µeq/l			
H^+	70	$SO_4^=$	77	H^+	61	$SO_4^=$	71
Ca^+	35	$NO_3^=$	41	Ca^+	33	$NO_3^=$	32
NH_4^+	34	Cl^-	8	NH_4^+	25	Cl^-	6
Na	21			Na	22		
Mg	8			Mg	7		
K	4			K	2		
TOTALS:							
	172		126		150		109

Points

i) From the bulk data, a comparison of the cationic balance to the anionic balance shows a no-charge balance. The same result is apparent from the wet only collectors.

ii) The hydrogen and sulphate ions are the dominant cation and anion respectively in precipitation in the area. They make up over half the deposition.

iii) The hydrogen to sulphate ion ratio is approximately a 1:1 ratio in terms of equivalents. Therefore, it is 2:1 in terms of a molar ratio.

iv) The wet concentrations range from 64% to 104% of the bulk concentrations. On average, the wet is 80% of the bulk, although this varies from element to element. A bold conclusion from this data, is that 20% of the deposition is in dry form.

v) The year-to-year concentration varies up to 1½ times the old.

vi) The variability from collector to collector ranges from 1 to 3 orders of magnitude.

Depositions 1977-1978

H^+	58	meq m^{-2} y^{-1}	Bulk	
	50	meq m^{-2} y^{-1}	Wet	
$SO_4^{=}$	64	meq m^{-2} y^{-1}	Bulk	3 gm.
	58	meq m^{-2} y^{-1}	Wet	2-8 gm.

These values are among the highest recorded on the Canadian Shield. As a comparison, the Experimental Lakes Area report H^+ as approximately 10 meq m^{-2} y^{-1} and $SO_4^{=}$ as 21 meq m^{-2} y^{-1}. Some seasonal pattern in deposition can be noted. Both the wet and bulk collection data show a higher deposition of $SO_4^{=}$ in the summer than in the winter. No significant trend was identified for H^+.

From the above information, we have obtained a preliminary idea of the importance of precipitation input to a lake. For example, I will use Harp Lake (data from 1977).

% Total Input to Lake from Bulk Precipitation

H^+	82%
$NO_3^=$	67%
NH_4^+	73%
Water	20%
Na	11%
K	9%
Cl	9%
SO_4	7%
Ca	5%
Mg	3%

The ratio of the lake area to the entire drainage basin is 13%.

LOU SHENFELD: What do these numbers add up to?

WOLFGANG SCHEIDER: 82% of the input comes from precipitation, i.e. watershed rain, etc. 13% of the elements are retained by the watershed either via the weathering process or taken up by the biota. The rest is from stream inputs. The results depend on the area, the watershed chemistry, and the stream data.

LOU SHENFELD: Can you explain why the $SO_4^=$ input is so low and the $NO_3^=$ is so high?

WOLFGANG SCHEIDER: The ammonia and nitrates are being retained by the terrestial watersheds. The sulphates enter the lakes from the streams. Since the lake is 13% of the whole watershed and if there were no interaction with soils, 13% of the input should be by rain. However, we have no measurements of solubility. Still we gauge the bulk deposition and the stream input.

MARY THOMPSON: I am worried that the lake is only 13% of the total watershed area but receives 20% of the rainfall.

WOLFGANG SCHEIDER: These figures show that water is being lost in the terrestial system before it enters the lake. There is more evapotranspiration than evaporation.

JIM KRAMER: Is there much iron sulphate in the area?

WOLFGANG SCHEIDER: No, there is not much iron sulphide in the area.

NELS CONROY: Did you account for any reactions in the other direction, i.e. sulphates ⟶ sulphides?

WOLFGANG SCHEIDER: No. We did not include that in our study.

HAROLD HARVEY: Is the data good enough to do a mass balance on the ion exchange?

WOLFGANG SCHEIDER: We are doing some. We have a good water balance on the lake and a good charge balance (within 7%).

PETER DILLON: How about H^+? Did you have the same problems?

JIM KRAMER: Is H^+ the most abundant cation?

WOLFGANG SCHEIDER: From the charge balance, yes.

JIM KRAMER: Did you use filtered samples?

WOLFGANG SCHEIDER: No.

JIM KRAMER: To measure insolubility by an analytical method, use Ca solid and increase Ca not measuring counterion.

WOLFGANG SCHEIDER: How do you test for that?

JIM KRAMER: Filter the sample and then do the analysis.

WOLFGANG SCHEIDER: That sounds partly like an analytical problem.

PETER DILLON: There was a significant amount of chloride.

DOUG WHELPDALE: Reject anything outside of 10%. Were your figures annual or 2 year?

WOLFGANG SCHEIDER: They were one year figures.

DOUG WHELPDALE: You get better results on a one-shot sample.

WOLFGANG SCHEIDER: That comes out in most of the samples.

WALTER CHAN: In Sudbury, the ionic balance was within 10%. It depended on the pH value from conversion of the field value in combination with the rest of the parameters.

PETER DILLON: Did this happen before the lab switched?

WALTER CHAN: It was after the switch.

PETER DILLON: You have a double estimate of sulphate.

FRANK VENA: pH measurements can change by 50%. It is difficult to state the true pH of a sample.

WOLFGANG SCHEIDER: We did variable collection of the samples, the average being from one to two weeks. The pH was measured at the lab at Dorset on the same day the sample was collected and then, the rest was sent to Toronto for the testing of the other parameters.

FRANK VENA: The hydrogen ion concentration is the major problem and also the low conductivity.

LOU SHENFELD: Did you do your comparison of bulk and wet data at one sampling station only?

WOLFGANG SCHEIDER: It was done as a grand mean for one year.

LOU SHENFELD: Is there little entrainment in the area? What is the underlying terrain like?

WOLFGANG SCHEIDER: The area is heavily forested and the stations are on the lake surface.

WALTER CHAN: Does the $SO_4^{=}$ correspond to 40% of the total loadings?

WOLFGANG SCHEIDER: Not enough to make a difference.

LEN BARRIE: That is the problem with H^+ estimates; they are not systematic.

FRANK VENA: Some balance and some don't.

JIM KRAMER: I suggest you filter the sample first.

c) Heavy Metal Deposition - D. Jeffries

For a more detailed discussion of this presentation, refer to Appendix Ten.

We currently have four stations monitoring for heavy deposition:

1.	Muskoka	-7 samplers
2.	Sudbury North (40 km.)	-2 samplers
3.	Sudbury Centre	-2 samplers
4.	Sudbury South (10 km.)	-2 samplers

While Mr. Jeffries was discussing seasonal trends in metal disposition, Mr. Martin asked the following question:

HANS MARTIN: Did you notice a change during the Sudbury shutdown period?

DEAN JEFFRIES: Yes, the values dropped off during the shutdown.

After the presentation (Slide 10) on the distribution of aluminum and iron, the following discussion occurred:

LOU SHENFELD: Your conclusion that if the background concentrations are lower, and if Sudbury and Muskoka-Haliburton had similar values, that the desposition falls out more quickly than copper or nickel is not necessarily true. An alternate conclusion could be that the background levels are higher.

DAVE BALSILLIE: The iron emissions are much higher and the source of this material is thought to be the new stack, related to out of stack or fugitive emissions. We found the same results from hi-vol and dustfall data; during the strike, the hi-vol and dustfall measurements of copper and nickel dropped off quickly.

DEAN JEFFRIES: Lou's question is difficult to answer because of differentiation at the source. Total input measurement cannot separate the two; however, entrainment dust does not appear to be a significant source.

DAVE BALSILLIE: Nels' lakes data show similar results for zinc and aluminum. The tests were not similar around Wawa since Wawa has no heavy metal problem like Sudbury - the problem there is with arsenic, manganese, and SO_2.

BOB VET: Did you obtain a similar pattern when the set deposition data was considered in relation to the bulk deposition data?

DEAN JEFFRIES: Wet-only data was only collected in the summer; the shutdown occurred in the winter. Copper and nickel showed a definite decrease but the other elements did not show any significant change.

BOB VET: What about the contribution of tailings?

DEAN JEFFRIES: They have an unquantifiable effect on the deposition numbers since they are converted to a wet slurry and then grassed over quickly.

BOB VET: What reports do you have on snow core sampling?

DAVE BALSILLIE: The blowing of tailings is a serious problem. At INCO the tailings are kept wet and non-grassed over areas are sprayed with a sealant. Non-active areas and embankments were revegetated which showed up on dustfall data. Then, during the strike, they were not spigoting the tailings which resulted in terrible dust storms in the spring. However, there should be no tailings problems in the Sudbury area now.

JIM KRAMER: Do you have an experiment set up whereby you can compare your on-water sample collector results to on-land ones?

WOLFGANG SCHEIDER: We currently have two micronetworks for just such intercomparison purposes. One network is on the surface of Red Chalk Lake and the other is located on the watershed. As regards the difference between deposition on-land and on-lake, we found more precipitation fell on lakes than on land but that the total deposition was higher on forests than on lakes as it is dropped down collectively.

d) National Atmospheric Chemistry Network - L. Barrie

Modellers need validation material in the form of simultaneous deposition and precipitation data. The Atmospheric Environment Service's network has been designed to serve just such a purpose.

For a map of the Air and Precipitation Monitoring Network (L. Barrie and A. Wiebe) refer to Appendix Eleven.

The following lists air pollution monitoring sites associated with long range transport:

	Network Site	In Operation Since
1)	Experimental Lakes Area - Schindler	Nov. 1978
2)	CANSAP	
3)	Long Pt., Lake Erie - Canadian Wildlife Service - M. Lusis, MOE	March 1979
4)	Toronto, CN Tower	July 1977
5)	Chalk River - P. Berry	Nov. 1978
6)	Kejimkujik National Park - J. Kerekes	May 1979

Activities:

1) Wet-only daily precipitation samples are collected at 8:00 a.m., bottled and stored at 4° C. They are analysed at CCIW to test for pH and major ions.

2) For the air sampling, there is 24-hour sampling for $SO_4^{=}$, $NO_3^{=}$, Na, K, SO_2. For low volume sampling there are two filters, the front filter is for particulates

whereas the back filter is for gaseous substances. These filters are shipped in monthly. We generally have eight filter paks and a dummy filter pak.

To date, we have concentrated on preliminary results from ELA in Kenora since November 1978. Sulphate particulates were graphed in $\mu g/m^3$ as a function of time. From the end of February into March, the sulphate concentration was elevated. We feel this was due to stagnant high pressure areas in the Chicago and St. Louis areas. There was more variation in NH_3 concentration than in SO_4 since ammonia is used in the pulp and paper industry. For SO_2, we found that the variation was great and that there was a high peak at the end of February and into March as well.

At the source, SO_2 is approximately 2% of the total sulphur emissions. The conversion of SO_2 to SO_4 is called the oxidation rate. We found a lot of variation in nitrate concentration.

A report on the first eight months of data is scheduled for January 1, 1980. This data will yield an understanding of which sources are affecting the air quality of which areas.

The SO_2 to SO_4 conversion ratio is important for long-range models. The short temporal variations are a good diagnostic tool for models as they will follow the actual air concentrations closely. $SO_4^=$ washout ratios are also important.

At the end of the above presentation, the following discussion occurred:

GREGG VAN VOLKENBURGH: Was it a site specification that the stations had to be placed along the border lakes?

LEN BARRIE: It was coincidental that they ended up along border lakes. The criteria for site selection were essentially good spacing and reliable manning of sites.

A. VENKATRAM: What SO_2 conversion rates do you use?

LEN BARRIE: As of February, 1979, 3%.

DAVE BALSILLIE: How long can you run a filter pak? I know that our passive samplers run for a week and if they don't work out, the filter paks run for 7-8 days.

LEN BARRIE: It all depends on the breakthrough of SO_2 which depends on the ambient concentration.

LOU SHENFELD: Did you do any comparisons with continuous SO_2 monitoring and 24 hour monitoring results?

LEN BARRIE: Just such a comparison process is currently ongoing at the CN Tower since we have a continuous SO_2 monitor sampling out of the same manifold.

MARIS LUSIS: You stated that you hoped that your event network data would enable you to determine which sources are contributing to which areas. How?

LEN BARRIE: One of our plans is to cut the particulate filters in half and analyze through Neutron Activation Analysis for trace metals to identify various sources such as the pulp and paper mill in Kenora.

MARIS LUSIS: What trace metals would you use to fingerprint smelter contributions?

LEN BARRIE: Oil generated.

MARIS LUSIS: How far distant is the ELA site from Thompson, Manitoba?

LEN BARRIE: Approximately 500 miles.

e) Great Lakes Basin

i) THE CANSAP NETWORK - D. Whelpdale

First of all, I will show the networks that are currently operating in the U.S.A. for data comparison purposes in the precipitation chemistry field.

Figure One of Appendix Twelve illustrates the location of the United States Portion of the World Meteorological Organization, the NOAA, the Environmental Protection Agency's Precipitation Chemistry Network sites. Figure Two of Appendix Twelve outlines the Electric Power Research Institute (EPRI) Precipitation chemistry monitoring network for the SURE study. Figure Three of Appendix Twelve outlines the EPA/DOE Multi-State Atmospheric Power Production Pollution Study precipitation chemistry network (MAP3S) which is a 24 hour event sampling network. The WMO is currently collecting monthly samples but is in the process of switching to weekly samples. Figure Four of Appendix Twelve details the National Atmospheric Deposition Project

Network (NADP) which collects weekly samples of precipitation and two monthly samples of dry deposition using an open bucket.

According to Liken's article in the October issue of Scientific American, his pH isopleths depict the expansion of the area affected by acid precipitation (See Figure Five of Appendix Twelve).

Figure Six of Appendix Twelve depicts pH isopleths based on the National Atmospheric Deposition Program's initial 1-6 month data. Figure Seven shows a comparison using the Canadian Network for Sampling Precipitation 1977 Data to determine pH isopleths in Canada (Figure Eight is similar but uses 1978 data). Both the 1977 and 1978 data are based on annual precipitation data averages and are very consistent.

To illustrate chemistry of precipitation changes across Canada, refer to Figure Nine of Appendix Twelve which depicts mean monthly concentration and deposition at Mount Forest, Ontario for July 1972 to April 1978. From the histograms in Figure Nine, we can see that sulphate and nitrate concentrations peaked in the late spring and H^+ peaked late in the summer. The deposition plots show the same conclusions.

Regional groupings were established based on the mean sulphate, nitrate, calcium and pH data for the period January 1977 - December 1978 (See Figure Ten*). Four main regions resulted, and Figures Eleven* and Twelve* show monthly precipitation weighted

areal mean concentrations of sulphate, nitrate, calcium, and hydrogen ion for these regions. For Region I, even with weighted mean values, we notice a definite spring peak in $SO_4^{=}$ and Ca. However, Ca peaked in the spring in several of the regions. The acidity peak moved later into the summer since the Ca^{++} would buffer the $SO_4^{=}$ and the NO_3^{-} until then.

In Figure Thirteen, the 'x' axis represents the ratio of wet to dry deposition and the 'y' axis represents the emissions per unit area of Sulphur. From the graph, we note that as emission density increases, the wet deposition becomes relatively less important and the dry deposition becomes relatively more important.

* Figures Ten, Eleven, and Twelve are the property of R. Berry.

Several questions were posed before Mr. C. H. Chan continued with his disucssion of the CCIW network.

LOU SHENFELD: Do you think your data is related to the elevation of the emissions?

DOUG WHELPDALE: No, although it might appear so due to the largeness of the regions.

LOU SHENFELD: Why does the Ca concentration drop off in the summer?

DOUG WHELPDALE: The ploughing of fields in the spring and the resultant dust leads to the high concentration of Ca in the spring. Once the ploughing stops, the Ca concentration drops off.

ii) THE C.C.I.W. NETWORK - C. Chan

In 1969, the International Joint Commission requested data on the loading into the lower Great Lakes. Since then, there have been many changes in the Great Lakes data base. In 1979, the I.J.C. objectives changed to read:

1. To estimate the contribution of the atmosphere to the chemical budget of the Great Lakes.

2. To establish long term records of chemical composition in the atmospheric precipitation in the Great Lakes Basin.

There are currently 15 monitoring sites involved in the C.C.I.W. network and most are located along the shoreline from Sydney to Kingston. The collectors consist of Sangamos, box samplers, or bulk-only samplers. The box samplers are not too satisfactory and are called snow samplers in the winter. The list of parameters for our samples consists of P, N, NH_3, Cl, major ions, pH, and some heavy metals (See Table I and see Figures One, Two, and Three of Appendix Thirteen for description).

DAVE BALSILLIE: What is the priority of these parameters?

C. H. CHAN: First nutrients, then major ions, and last, trace metals.

At the beginning we concentrated on the lower Great Lakes, but the network was extended to Sydney in 1977. However, we still have

insufficient data to allow for interpretation. Figure Four outlines the location and types of samplers in the CCIW network.

DAVE BALSILLIE: How do the Sangamos compare to the rain and snow samplers?

C. H. CHAN: Burlington is the only station set up for this comparison, but it is not the best station for such a comparison (See Figures Five and Six).

The remaining Figures and Tables in Appendix Thirteen show some very interesting inter-station comparison values. From the data in Table II, 1972-77 Lake Ontario Precipitation, the Kingston, Trenton, and Woodbridge conductivity figures are generally lower than those for Toronto and CCIW. We also see in general, higher concentrations of nitrates at these two stations. This difference can be attributed to the fact that the Toronto site is located at Centre Island airport and the CCIW site is located below the Skyway Bridge where heavy traffic would result in a higher concentration. Still it is not consistently higher than the other areas, and an alternate explanation is that the nitrate must have undergone some transformation. The Toronto and CCIW stations also have higher concentrations of Na, and Cl which could be attributed to the use of road salt. They also have a higher concentration of sulphates.

The last Figures in Appendix Thirteen consist of seasonal and yearly variations of several parameters. The seasonal variation (1972-1974 data) of p. 11 is similar for Kingston,

Trenton, and Woodbridge. Toronto and Burlington have a different seasonal variation. It was also noted that the samples from the Toronto and Burlington stations contained some algal growths, perhaps indicative of nitrogen depletion in the summertime.

MARIS LUSIS: When did the sulphate concentrations peak?

C. H. CHAN: Either in August or in October.

MARIS LUSIS: Those peaks are different from CANSAP's data.

Some points that were mentioned before closing were 1) that when the loadings for the 5 data stations were computed, the information seemed biased to Toronto and Burlington due to local effects in these areas and 2) that the bulk samplers indicated higher pH than the Sangamos.

SERGE VILLARD: Do you envisage any major changes in the Great Lakes Network?

C. H. CHAN: Yes, the shift in emphasis will be to use more Sangamos.

f) Alkalinity Methodology as Related to Soft-Water Measurements - S. Villard

Mr. Villard discussed the various changes that have occurred in the methodology of measuring alkalinity with specific reference to the Ministry of the Environment. Reference was also made to the calibration of the various methodologies. (See Appendix Fourteen).

In conclusion, Mr. Villard stated that currently an intercomparison study between MNR and MOE and U. of T. low level alkalinity data is underway in order to assess the validity of the various sampling methodologies.

At this point in the presentation, the following interchange of information occurred:

MARY THOMPSON: For the soft glass experiment, what cation accelerated the soft water leaching of bicarbonate?

SERGE VILLARD: Sodium.

FRANK VENA: The experimenters were essentially interested in the various properties of the containers.

MARY THOMPSON: Did the glass bottles have a high silica content?

SERGE VILLARD: I don't know but I can find out for you.

LEN BARRIE: Did you test polypropylene and polyethylene?

SERGE VILLARD: No, but we had several previous bad experiences with those two substances.

PETER DILLON: What was the mathematical relationship between alkalinity measured to final endpoint and any other measured alkalinity?

SERGE VILLARD: Such a relationship is difficult to determine due to the inaccuracies of the pH meter. The final endpoint might read as 4.5 but could still be 4.7.

PETER DILLON: Then, theoretically you cannot predict TIP alkalinities vs. fixed endpoint.

JIM KRAMER: For gran titration, you do not have to calibrate your pH meter because the linear relationship holds.

3. Open Discussion

Jim Kramer, the chairman for this session, noted several points which were then raised for discussion.

1. Do you feel that there are currently too many parameters being measured, or that others are needed?

2. What is the future longevity of the individual study programs?

3. How is the intercomparison of results handled, and is this method acceptable?

4. Is the design of samplers still a problem, or do you think that the state of the art is adequate at the moment?

5. Due to the various methods of data collection and documentation, do you feel we need a unified data depository?

POINT #1: Parameters

LEN BARRIE: Two comments. We are not measuring the hydrogen ion concentration, and we should be. As well, we are using particulate filters that affect pH.

SERGE VILLARD: There are too many networks, and each essentially has been established for a different purpose.

NELS CONROY: I think we have a tendency to over-measure and that we are reluctant to stop collecting data. We need more replicate measurements of fewer parameters.

LOU SHENFELD: With the cellulose filter, there is no SO_2 impingement as with the glass fiber filters. However, we must remember the principal purpose of the monitors.

MARIS LUSIS: There are two types of filters when analyzing for sulphates. The intercept is at 5.0 $\mu g/m^2$ and since this difference is constant, we need only subtract 5.

FLOYD ELDER: The difference is that CANSAP and NADP are not geared to nutrients while CCIW is geared to nutrients. There are also differences in the total metals and in filtered and non-filtered samples.

MARIS LUSIS: For wet-only samples, we do unfiltered ones.

C. H. CHAN: Unfiltered samples.

DOUG WHELPDALE: Unfiltered samples. NADP does filtered.

JIM KRAMER: For unfiltered samples, I do not see the validity of doing a charge balance.

LEN BARRIE: For the sampling method for metals, the way to preserve them and prevent loss is by acidifying the sample.

MARIS LUSIS: We seal the sample bag and send it to the laboratory for analysis for metals. With the S.E.S. samples in acidified containers, we have noticed some leaching of the walls.

POINT #2: Longevity of Individual Study Networks

Sudbury Environmental Study	- 1980
Acidic Precipitation in Ontario Study	- long-term
Experimental Lakes	- long-term
CANSAP	- long-term
APN	- 3-5 years
CCIW	- unknown

POINTS #3, 4, 5: Intercomparison of Results, Sampler Designs, and Data Depository

GREGG VAN VOLKENBURGH: All networks employ the same samplers with subtle and non-subtle changes in design, e.g. the use of a silicon gasket to cut down on the amount of evaporation. But the problem is, can all the networks' data be fed into a common depository such as NAQUADAT? Is anyone here on the committee?

DOUG WHELPDALE: Yes, since 1973.

LOU SHENFELD: Is it possible then to standardize all the data?

GREGG VAN VOLKENBURGH: The NADP currently has a contract out for the documentation of their sites and methods to determine how well they correspond to Ontario Hydro's.

DOUG WHELPDALE: The problem seems to be that agreement as to the best procedure cannot be reached.

FLOYD ELDER: A report is scheduled to come out in November that will document U.S. and Canadian sites and procedures.

SERGE VILLARD: The information stored should include what has happened to the various networks and any changes that have occurred in these networks.

JIM KRAMER: Where will this information be stored?

DOUG WHELPDALE: CCIW and CANSAP data are already stored in NAQUADAT. Has anyone present ever tried to extract data from NAQUADAT?

LAURA JOHNSON: A few years previous, documentation was a problem. The recent data is easier to access. We need to make a concerted effort that enough parameters are available so that the data will still be useable in the next ten years.

JIM KRAMER: How does one achieve access to a file, and how complete is the stored data?

FLOYD ELDER: There is a different code to show where the data can be obtained.

DOUG WHELPDALE: The EPA SERODS system is used for precipitation chemistry data for long-term networks. For example, in the case of the NADP, there would be leader fields for

methods and site locations and then the actual data, conversion factors, periods of operation, etc. can be accessed. Could we duplicate such a system in Canada?

GREGG VAN VOLKENBURGH: Why don't we buy SERODS?

DOUG WHELPDALE: The long-term will be a limiting factor.

4. Session Recommendations

1. A Federal/Provincial deposition effects working group should be established.

2. This group should be charged with the responsibility of:

   (i) Establishing and maintaining a central date clearinghouse and repository.

   (ii) Gathering together all data from all currently operating networks, standardizing it where possible, and making it available to the research community from the central repository mentioned in 2 (i).

   (iii) Standardizing all current and proposed network sampling methodologies where possible.

   (iv) Eliminating network redundancies where possible.

3. Basic experimental work on wet and especially dry deposition methodologies should be encouraged and supported.

C. SESSION 3 - Susceptibility and Regime Response to Atmospheric Loading

1. Session Introduction - H. Harvey

A better integration of studies is currently necessary. Many times recently I have read or heard this statement, "Acid rain kills fish". This statement should be changed to read, "the causality could be inferred that increased acidification of lakes is accompanied by a decline in fish".

To demonstrate why a lake is acidified an H^+ balance has to be constructed. Such a balance is needed to prove the case that acidification results in loss of fish and biota from lakes.

Drs. Van Loon and Beamish constructed an H^+ budget for Lumsden lake. They measured the pH of the lake seven times and also measured the pH of the rainfall. However, their resultant annual budget is not satisfactory since it is incomplete. The inflow was monitored mainly during one month, April, and caused a discrepancy in the inlet and outlet pH. This budget would need more data as well as more detail in the data.

Another example is the Adirondack paper where 217 lakes were sampled and a histogram of lakes distributed by pH was drawn up. Forty out of these 217 lakes surveyed in 1930 showed a significant shift to lower pH and less fish in the 1970's survey. This paper again invites the reader to conclude that acid rain kills fish.

A Norwegian paper which has a title of "Fish Kill and Low pH" when translated into English, also infers the same conclusion. In this paper (English version) five stations were monitoring the Tobdal river during the time of the fish kill and measurements on the blood chemistry of fish plasma for Na + Cl indicated a high hydrogen loading. In the original Norwegian version of the paper, the fish died between January and March under the ice, but the researchers did not carry out their fish survey until April and May - not until after the event. (There are some fish that were from the site where the fish died earlier that are still alive.) When the fish were taken from the river and exposed to a pH of 4.0 or 6.0, their blood chemistry (Na/Cl ratios) were studied for an indication of trouble. However, some fish that had indicators of trouble and were exposed to a pH of 4.0 did not die.

Is all the above data enough evidence that low pH kills fish? I, personally, think it's pretty poor.

2. Presentations

a) Effects of Acid Precipitation on Terrestrial Systems - S. Linzon

Overview and Preliminary Results

The effect of acid precipitation on lakes and fish poses a real and immediate problem; however, the effect of acid precipitation on soils and vegetation is a potential threat. The order of sensitivity to the various

pollutants involved is: rain, lakes, fish populations, soils, and vegetation.

Regarding soils, there are a number of processes in addition to atmospheric deposition that lead to soil acidification, such as:

1) carbonic acid formation due to respiration of soil organisms.

2) mineral acid from nitrification.

3) organic acid from plant residue decomposition.

4) oxidation of pyrite through aeration.

5) inputs of acidifying substances from the atmosphere.

Both short-term experiments using severe acid loadings and highly acidified water and long-term real situations such as continued exposure to emissions of nearby point sources show similar results on soils. Some of these results of acidity are:

1) leaching of the basic cations such as Mg, Ca.

2) reduction of cation exchange capacity.

3) mobilization of aluminum, iron and other ions.

4) changes in biological activities such as reduced nitrogen fixation and/or nitrification.

Whether or not these effects are occurring as a result of current acidic precipitation is not

fully known at this time since we have no direct proof and many years of study are required.

At the May 1978 Nato meeting in Toronto, the effects of acidic precipitation on terrestrial ecosystems were discussed. The conclusion reached was that acid precipitation could affect certain physical and chemical soil properties such as base saturation, cation exchange capacity and humidity. However, no hard evidence currently exists to show that these changes exist due to acid precipitation. The need for long-term studies under realistic acid loadings and contrarily, short-term studies under high acid loadings to shorten the timescale involved is definitely apparent.

At present a controversy exists as to which soil type is most susceptible to change by acid precipitation. One would assume that acidic soils that lack buffering capacity would be most susceptible, i.e. podzolic soils. A Swiss researcher discovered the contrary. Since the H+ exchange sites were already occupied, these soils are not sensitive. Calcareous soils are the least sensitive and non-calcareous sandy soils with a pH over 6.0 are the most sensitive.

In 1960 a soil survey was carried out in the Parry Sound area by University of Guelph students. After an 18 year period, a similar survey with the same objectives, to sample soil profiles and collect pH measurements and at the same site locations was undertaken. The pH results were then compared to the 1960

data and there was little change. Any differences could be attributed to differences in measuring methodology. The soil horizons were normal with a low pH at the surface and an increase as one goes down.

One problem that it is appropriate to mention at this time is the different classifications of soil types in Canada and the United States. This issue will have to be resolved to make comparison of data feasible.

The Magnetawan clay soil pH measurement ranged from 5.7 deeper to 4.8 at the surface. This soil was the only one measured at a pH of 5.0 in 1960. The original measurement is questionable. The podzolic sandy soils had the lowest pH. These tests are consistent with Wicklander's in Sweden who had similar results on podzolic soils - no changes over 39 years. The conclusion reached is that once a soil is highly acidified, it has no opportunity to become adversely affected by acid precipitation. Perhaps the intermediate soils between acidic and calcareous are the most sensitive.

Another aspect in this issue that should be studied is the influence of the soils on the acidic precipitation en route to the lakes. Is it changed in any way? Results from such a study might account for several discrepancies such as two lakes that are side by side with a different pH even though the amount of acidic precipitation deposition is the same. The terrestrial systems surrounding the lakes may

prove to be a factor for such a discrepancy.

Another component of a terrestrial system is the actual vegetation. Vegetation is less sensitive than soils. (Note: Terrestrial systems are more complex and heterogenous than aquatic systems; therefore, to neutralize them would also be more complex.) At the moment, there is no direct proof that acidic precipitation is causing adverse effects on vegetation either directly or indirectly through soil acidification. In controlled experiments using simulated acid rain with a pH of less than 3.4, a number of effects on vegetation have been reported including leaf cuticular abrasions, leaf lesions, and the leaching of nutrients from the host. However, these effects are difficult to demonstrate in the field on natural vegetation.

Jacobsen and Van Leuken at Cornell University initiated several such experiments and their conclusion was that there was little risk of injurious effects on natural vegetation because the pH of successive rain events is rarely below 3.8.

In 1972, it was reported in Stockholm that acid precipitation caused from 0.3 to 0.6% loss in forest productivity. However, Dr. Tamm refuted this claim in Ambio, (Vol. 5, No. 5-6, pp. 235-238, 1976), stating

that there was no direct proof linking acid rain to loss of forest productivity. The issue is further complicated by the fact that there is great individual variation in tree growth depending on weather, climate, site, and soil type. Wicklander also disagreed based on the fact that most soils have a pH of less than 5.0 naturally and therefore, acid precipitation is unlikely to have an effect on vegetation. Cogbill observed no decrease in productivity in the Northeastern United States and Tveite and Abrahamsen in Norway actually found that tree growth was stimulated by acid precipitation. Bormann's conclusions (that there are a number of compensatory factors to acid precipitation) were substantiated by six other studies. These factors include increased leaf falls, weathering of rocks, mineral uptake and soil replenishment.

From all the above statements, I feel that we cannot remain complacent and wait until the effects are evident. By that time it will be too late.

Studies and development in the following areas are needed now:

1) surveillance and monitoring of baselines and trends in Ontario.

2) determination of the most susceptible soils.

3) determination of the effects of soils and vegetation on rain en route to lakes.

4) development of protective or remedial measures.

At the conclusion of the above presentation, several attendees questioned the speaker.

DOUG WHELPDALE: What is the actual extent in Ontario of the soils thought to be most susceptible?

SAM LINZON: We are currently looking into this area. Even though there has been some soil type mapping by the University of Guelph and M.N.R., it is not sufficient to give an exact figure. The non-calcareous, sandy soils are thought to be the most susceptible, but we are not sure of the extent of this soil type throughout Ontario.

DOUG WHELPDALE: Could you give me a percentage estimate?

SAM LINZON: I would say approximately 10%.

MARY THOMPSON: In the resurvey of the Parry Sound area, was any greater thickness of the A layer noticed?

SAM LINZON: I don't think there was too much difference; however, we have only really looked at pH so far. We plan to do more comparisons of other parameters since the 1960's work is very well described.

TOM BRYDGES: I thought the soils would have to become acidic before the streams and lakes would become acidified. Why are the soils less susceptible?

SAM LINZON: The answer lies in the effects of various soil types on precipitation. When the soil is thin with a pH of about 4.0, the water runs straight to the lake leaving the pH unchanged. However, if it is a thick calcareous soil type, the pH of the precipitation could be increased before actually entering the lake.

TOM BRYDGES: How can the soils and forests still be in such good shape, when so many streams and lakes have been damaged by acid precipitation?

SAM LINZON: Soils do not change rapidly. Perhaps we have an ideal situation here, where the acid precipitation runs straight into the lakes with no changes.

b) Lake Hydrology and Acid Loading - W. Scheider

Last evening Dean and I talked a bit about the precipitation work we are doing. This morning I'd like to put it in a larger context.

One of the objectives of our program is to measure mass balance parameters and use them to predict the rate of acidification of softwater lakes.

We currently have two study sites, one in Dorset and one in Sudbury. These sites were chosen partly for historic reasons, i.e., we have ongoing programs at those sites. The Sudbury site is part of the S.E.S. program looking at the effects of the smelting industry on the area. We have seven lakes under study

at the Sudbury site. The Dorset site is part of the Lakeshore Capacity Study whose objective is to study the effect of lakeshore development on lakes. We presently have 15 lakes under study in this area. The A.P.I.O.S. core set of lakes from the two sites will total 13, eight from Dorset and five from Sudbury. All these study lakes are susceptible and their pH's range from 6.7 to 4.1. However, the Sudbury acid lakes are atypical of acidic lakes.

We have a good data base at these lakes: S.E.S. since 1974 and L.C.S. since 1976. Much of the information will be very useful.

Measurements Taken

Besides standard lake morphometry measurements, we have studied the bedrock and the surficial geology and have reported some small-scale variations. (I would emphasize that the available provincial maps for this purpose are not detailed enough for our needs which are to try to understand the nutrient and ion export.) Our meteorological measurements will help us to develop a lake evaporation model and an evapotranspiration model. I discussed the precipitation chemistry models yesterday. Our essential interest is in chemical and biological estimates. Our routine and biological chemical measurements include nutrients, major ions, heavy metals, phytoplankton biomass and zooplankton biomass. Some non-routine measurements are sedimentary chemistry, nutrient kinetics, and primary production.

Stream and Hydrology Work

This area involves our budget work for water and other materials. The main avenues of

input into a lake are direct precipitation and stream inflow. Currently we have 35 weirs and flumes on major outlets and inlets of seven lakes in the Dorset area.

A typical hydrological site would usually include a V-notch weir, a stilling well, a flow recorder, and means of continuously measuring the water height. As a result stream inlet and outlet flows can be monitored.

In Sudbury, similar sites are being constructed and the new weirs will be made of cement not plywood, but they will have the same afore-mentioned accoutrements.

Once we have collected the data over a period of time, we work it up in the following manner. We make a plot of the mean daily discharge of the lake which shows the temporal variability in stream flow. From these plots we discovered that the spring and fall months are seasonally important. We also study annual variability which shows us for example, that in 1977 we had a very wet fall with only half the input in March and April.

There are different ways to work up the data collected which will, of course, give different results. In the daily discharge measurements there is 0% of error but in instantaneous measurements you may have a range of answers that differ by 30%. Since there are several ways to work up the data, all the researchers in this area should agree on one method. If, however, you have no hydrological data, and work the model using only precipitation and evapotranspiration, you may be off by 70%.

Table One

HARP LAKE

Budget 1977

	2 yr. INPUT	3 yr. EXPORT	meq/m^2/yr. NET
Ca	31.4	80.8	49.4
Mg	7.5	38.9	31.4
Na	17.3	21.0	+ 3.7
K	3.5	5.6	2.1
NH_3	26.4	1.7	-24.7
"H"	56.4	1.7	-54.7
Σ_+	142.5	149.7	
SO_4	62.9	109.8	46.9
Cl	7.7	10.4	2.7
NO_3	29.3	4.2	.1
HCO_3	0.0	36.2	36.2
Σ_-	99.9	160.6	

For the conservative ions such as Ca, Mg, Na, input should equal output.

MARIS LUSIS: Did you account for any ungauged means of outflow?

WOLFGANG SCHEIDER: Most of the input into a lake comes from either precipitation or streams. However, not all watersheds are drained by streams. Small outflows can occur that cannot be gauged. Therefore, we take the average export from gauged streams and apply it to ungauged areas (using geological maps). To begin with, though, we try to select lakes where all input and output avenues can be monitored.

Average Harp Lake Watershed

The input figure of precipitation to Harp Lake is documented for a two-year period. The export figure is for the average watershed (weighted watershed data accessible to area) and has been documented over a three-year period.

Results:

1) The Na, K, and Cl input to the watershed closely balances the loss by the watershed (within approximately 3%).

2) There is a net uptake of NH_3^+, $NO_3^=$, and H^+ by the watershed; for example, approximately 25 meq of nitrate ($NO_3^=$) were retained by the watershed. The watershed retains substances for uptake by plants and soils. The H^+ uptake can be explained by uptake for weathering processes and outflow in a different form.

3) The loss of bicarbonates is less than half the loss of Ca and Mg. One would expect a loss of bicarbonate to balance the loss of Ca, Mg and H^+ ion retention but the above result shows strong acid weathering occurring on these watersheds.

4) The amount of sulphate is very disturbing since there is not much pyrite (sulphur bearing rock) in the area. Therefore, we may be overestimating the $SO_4^=$ in streams and underestimating the $SO_4^=$ in precipitation. We may be having the same analytical problems since we switched methods.

At the end of this presentation the following discussion occurred:

JIM KRAMER: The $SO_4^=$ plus HCO_3^- is approximately equal to Ca plus Mg. Can there be a $CaSO_4$ source which combined with the weathering of calcium carbonate accounts for this? The $SO_4^=$ figure is very interesting.

DEAN JEFFRIES: Could there be a $CaSO_4$ source?

JIM KRAMER: Not in Southern Ontario.

PETER DILLON: When $SO_4^=$ output exceeds the input, that is typical of dystrophic watersheds. The literature documents such types of phenomenon.

LEN BARRIE: What errors are placed on these numbers?

WOLFGANG SCHEIDER: I can only give you a general conclusion.

LEN BARRIE: Equal to 50% of 149?

WOLFGANG SCHEIDER: The errors on this is greater than others. We never followed through with an error type analysis but built in possible errors.

SAM LINZON: Part of your answer to the sulphate question may lie in dry deposition. The deduction in Norway is that wet or dry deposition of $SO_4^=$ is added during showers. The dry deposition of SO_2 is absorbed by vegetation and via a heavy rainfall washed into the lake.

WOLFGANG SCHEIDER: How much direct SO_2 deposition is there in this area?

LEN BARRIE: We assume set limits from the ambient air quality, then estimate typical deposition velocities to watersheds.

NELS CONROY: What are typical numbers for the percentage of sulphate in the air?

LOU SHENFELD: The SO_2 levels are low in Dorset, the background level is less than 1 µg/l.

LEN BARRIE: From Chalk River.

A. VENKATRAM: Single numbers are present in deriving averages but it is necessary to derive the variance. Changes might be low if variance is high.

WOLFGANG SCHEIDER: Yes, I agree. However, we have numbers for all study watersheds and they all show the same trend. I cannot give the changes at this time.

A. VENKATRAM: Changes might be large.

JIM KRAMER: SO_2 deposition estimates must be available for lake deposition and land deposition. But that still does not account for your SO_4 figures; (even if we use data from leaf uptake) we can eliminate direct uptake.

WILFGANG SCHEIDER: The precipitation data is based on monitoring of lakes and in open clearings. We omitted leaf uptake data.

DOUG WHELPDALE: 5 $\mu g/m^3$ SO_2 deposition would be adequate to bring up your budget. (30 meq $/m^2/yr.$)

JIM KRAMER: That is at 100% conversion.

LOU SHENFELD: You still have a low level in that area.

LEN BARRIE: The background level is less than 1 µg/l.

c) Preliminary Results of Lake Susceptibility Surveys - J. Allin

Those of you who were at the First Workshop in Sundridge will recall that one of the major needs identified was the need for good alkalinity data in Ontario.

There is no shortage of alkalinity data as such, but there is a shortage of good alkalinity data -data sufficiently accurate to allow an assessment of the potential susceptibility of lakes across the Province. Most of the existing data, my own Ministry's included, is total fixed endpoint alkalinity and has low precision at that. As Serge Villard explained yesterday, this kind of data is unreliable, particularly in softwater situations.

Also at Sundridge, the Ministry of Natural Resources was identified as the appropriate group to collect alkalinity data on an extensive basis. This decision was based on the following:

1. We have a long-standing lake inventory program in which 600-700 lakes are surveyed each summer; so, we already have a data base for many of these lakes.

2. These surveys are done by students who visit each lake only once (during the field season from May to August). They collect basic water chemistry and habitat information and determine the species of fish in the lake.

In order to modify this program to obtain better alkalinity and pH data, we had to upgrade our equipment and methods. As a result, for the summer of 1979 we obtained good quality pH meters and Burettes, and did Gran analysis on the results for total inflection point alkalinities. We could not afford to equip all of our crews this way, but we did have nine sets of equipment operating. Sampling was done using a plastic tube to collect water from the surface to the bottom of the thermocline, i.e. a non-weighted composite sample.

The work this past summer was concentrated in two main areas:

1) The Algonquin Region from Georgian Bay through to the Muskoka and Haliburton regions including Alqonquin Park.

2) The Northeastern Region including areas around Blind River, Sudbury, and Temagami.

More limited work was also done in an area west of Thunder Bay by Dick Ryder, a member of our research staff.

Most of the work was done by students but there was some participation by research people and Algonquin F.A.V. One of the crews in Algonquin ("roving crews") devoted all its time to collecting water samples and measuring pH and alkalinity and did not participate in the regular survey program. As a result, it was able to sample a large number of lakes.

Still, there was some concern raised about quality control, especially where a large number of student crews were involved; so, we ran a number of comparisons with M.O.E. on the same lakes. Additional samples will be taken but the results to date seem to compare very well.

I do not have a final total on the number of different lakes sampled but the figure will be over 250. Most of these lakes were only sampled once, but some such as Opeongo were sampled several times throughout the year. For the one-shot samples, we will not be able to determine any seasonal trends or the acid pulse at spring runoff.

The results have to be considered as preliminary at the moment as we have not done a thorough analysis yet, but I can at least report some general idea of our findings.

The following is a brief review of the results for eleven different tertiary watersheds on which we have the best sample size - approximately 200 lakes.

(For diagrams, see Appendix Fifteen).

1) A great majority of these lakes are potentially susceptible to acidification. 84% of these lakes had an alkalinity of less than 300 µeq/l (15 ppm $CaCO_3$). In fact, in the majority of watersheds, every lake tested had an alkalinity of less than 300. For example, in a watershed to the east of Georgian Bay, 29 out of 30 lakes had an alkalinity less than 300 and 70% were less than 100. The pH ranged from 5.0 to 7.5 with the majority between 6.0 and 7.0.

Another example, fairly similar to the previous one is the Sturgeon River watershed draining into Lake Nipissing. All 24 lakes had an alkalinity below 300 with over 60% below 100. The pH ranged from 4.5 to 7.5.

2) One exception to the above rule was the Camaron Lake Watershed through Minden to the Kiwarthas. It appears to have a significantly different distribution of alkalinities. Here 45% of the lakes had alkalinities over 3,000 µeq/l and the pH's ranged from 5.5 to 8.0. Therefore, there are more lakes here with better buffering.

On closer inspection, it was discovered that most of the higher alkalinity lakes were in four townships in the Northeast section: Dudley, Monmouth, Glamorgan and Snowden. This data is consistent with the geology of the area since almost all of these lakes lie within limestone outcrops. The relationship between geology and alkalinity needs to be looked at much more closely, but at first glance it appears to be a sound relationship.

The most alkaline lake we found was North Chain Lake in the Upper Madawaska River watershed; its alkalinity was 2850 µeq/l (142 ppm $CaCO_3$) as it was surrounded by limestone.

In conclusion, I would like to say that we intend to continue and expand the program next year in order to increase the data base across the province.

After Mr. Allin's presentation, the following discussion occurred:

SAM LINZON: Is your data base to be put into O.F.I.S.?

JOHN ALLIN: Yes and the data will also be kept by the Water Resources Branch.

FRANK VENA: Is Big Cedar Lake with its high alkalinity in the same area?

JOHN ALLIN: There are several pockets of limestone there but I'm not certain. However, it fits well with the geology.

NELS CONROY: I would like to make the following comment. It is encouraging that after the Sunridge Conference the M.N.R. responded to the needs identified there so quickly to come up with a new data base. The people involved really deserve a lot of credit.

MURRAY JOHNSON: In this survey, was the contribution of geochemistry taken into account? Lakes with various degrees of dystrophy contribute to their potential for buffering inputs.

In the E.L.A. study, nutrients acted differently than expected in dystrophic and non-dystrophic lakes. The dystrophic properties affected the results.

The answer to this question was deferred.

MARY THOMPSON: What was the effect of nutrients on dystrophic lakes?

MURRAY JOHNSON: Humic acid and sub-neutral material formed.

SERGE VILLARD: Will the M.N.R. test these lakes again or move on to other areas?

JOHN ALLIN: We will move on as there are large areas still to cover. The area will be decided on after discussion by the technical committee.

JIM KRAMER: Besides pH and alkalinity, did you measure any other parameters?

JOHN ALLIN: Yes, we also measured conductivity.

LOU SHENFELD: Was an adjustment made for seasonal change since some lakes would have been sampled in May and others perhaps in August? Did you adjust to make the data comparable?

JOHN ALLIN: I'm not aware of any method to adjust for seasonal variability.

LOU SHENFELD: Did you mark the month of sampling?

JOHN ALLIN: Yes, we did.

HAROLD HARVEY: The date does not do any good.

DEAN JEFFRIES: The goal of the program was to obtain a broad-based data package on a large number of lakes. Other groups are doing studies on temporal variations. Also, the samples are composite and not just surface samples so they give a reasonable representation of what is in the lake. Hopefully from this data we will be able to predict parameters when given appropriate geologic parameters.

JOHN GUNN: A Sudbury lake survey crew did parallel samples on Nelson lake to compare with M.O.E. samples to see if we could key into the long-term sampling study.

d) Aquatic Setting of the Algoma Lake Watershed - J. Kelso

For a detailed outline of this presentation see Appendix Sixteen.

At the discussion of pH on Page 2 of Appendix Sixteen the following question was asked.

LEN BARRIE: Is that an arithmetic mean pH value or H^+ average?

JOHN KELSO: It is a measurement of pH from the hydrogen ion using our own measurements from bulk collectors. The data is lognormally distributed.

This presentation leads logically into the next two presentations, so questions were deferred until the total package on the Algoma watershed was completed.

e) The Chemistry of the Turkey Lake Basin - F. Elder

One has to give John Kelso credit in his selection of a Study site since 100 sites in the Algoma area were visited before the Turkey Lake basin was selected.

The Turkey Lakes comprise a 443 hectare drainage basin with an average pH of less than 6.0. The total basin is 1,000 hectares. (See Figure 1 of Appendix Seventeen for location of lakes in basin).

Since no hydrographic studies were done on the study, we used the data from the Batchawana River. From one summer of measurements, we assumed the following:

Rainfall	100 cm. (longterm mean)
Basin Yield	58 cm.
Concentration Ratio	1.72

RAIN CHEMISTRY (BATCHAWANA BAY)

$SO_4^=$	2.75 mg/L	57.3 µeq/l
Ca	0.313 mg/L	15.6 µeq/l
$NO_3^=$	0.492 mg/L	
pH	4.37 mg/L	42.1 µeq/l

Ca yield Basin whole		3492 mg/y/m^2
Rain contribution		313 mg/y/m^2
Net Erosion from Basin		3179 mg/y/m^2
	=	159 meq/y/m^2

H^+ loading	42 meq/y
Ca yield from Upper Basin	65.8 meq/y/m^2

*The basin is not able to yield cations at a greater rate than the demand of the H^+ loading.

All the above estimates are based on very tentative assumptions.

1. Basin yield = Mean Batchawana yield
2. Water chemistry ≠ Σ of hydrograph

The following details the alkalinity and $SO_4^=$ measurements for the upper two lakes in the basin.

Lake	Alkalinity	Sulphates
#1	less than 50 µeq/l	138 µeq/l
#2	approximately 100 µeq/l	138 µeq/l

(See Figure 2 of Appendix Seventeen for data on lakes further down the basin).

To obtain the sulphate data, we compared the loading with the discharge, allowing one year of residence time. From Figure 2, one notices that alkalinity increases as one goes down the basin, but the sulphates remain approximately the same. Therefore, the terrestrial effects are apparent.

Figure 3 shows an alkalinity deficit of 100 µeg/l. Since the alkalinity is not as high as expected from the calcium available, the rainfall of pH=4.0 must have some effect on the situation. Loss of alkalinity due to acidification is indicated.

From the data I've shown, I'm sure you will agree that this basin is an interesting one for study purposes but will also prove difficult for achieving an adequate water budget.

PETER DILLON: Are these high calcium yields reflected in elevated calcium concentrations in lakes? Are the summer measurements higher than annual?

FLOYD ELDER: What are elevated calcium concentrations?

PETER DILLON: If you use your figure as the annual concentration, then a simple one-box model will give your calcium yield.

FLOYD ELDER: My estimates may be totally wrong as I have few data to input-mean annual hydrograph and summer data.

HAROLD HARVEY: When will the field station be ready for visitors?

FLOYD ELDER: It is accessible now with a four-wheel drive vehicle. Field quarters will be set up next spring.

Further questions were deferred until the next presentation, which is related to the previous two, is completed.

f) Terrestrial Environment of the Algoma Watershed Study - I. Morrison

The study area is 50 km north of Sault Ste Marie which has a minor point source, the coke ovens at A.S.C. The site area is also 100 km south of Wawa where there is a significant point source, the A.O.D. sintering plant. However, the prevailing winds are from the southwest and carry the Wawa plume to the northeast. The study area is also 25 km east of Lake Superior (Mamainse Point) and 13 km inland from Batchawana Bay.

The topography of the area is quite rugged. Some typical elevations are:

Lake Superior	184 m.	-	603 ft.
Turkey Lake	350 m.	-	1,150 ft.
Headwater Lake	490 m.	-	1,600 ft.
Batchewana Mtn.	640 m.	-	2,100 ft.

The watershed outflow is circa 400 ft. higher than Lake Superior. There is 1,100 ft. of relief within the watershed.

The bedrock geology consists mainly of large swatches of granite and belts of greenstone.

Greenstone (metamorphic rock, salt derived, chlorite schist) 93%

(Archean) Granite (some sp. biotite, hornblend granite) 7%

At this point, I will give a lake and terrestrial summary. The overall area of the site is approximately 1,400 ha. There are six lakes in the site, five in one chain plus a sixth that is apart. The lakes range in size from circa 5 to 54 ha. The greatest proportion of the area (84%) is in merchantable forest.

LAKE AND TERRESTRIAL SUMMARY

Lake Summary	Area (HA)	
North Headwater	11.8	
Second	18.8	
Beaver Pond	4.7	
Little Turkey	20.4	
Turkey	54.4	
South Headwater	5.3	
Lake Total	115.4	8%

Terrestrial Summary

Timber Forest	1,192.8	
Protection Forest	86.9	
Open Wetland	18.2	
Terrestrial Total	1,297.9	92%
Total Watershed	1,413.3	100%

FOREST REGIONS

The zone of depressed pH is largely contiguous with the Great Lakes - St. Lawrence Forest region. This region typically contains tall hardwoods specifically hard maple (66%) and yellow birch (approximately 20%). A light selection of these trees were cut in the mid-1950's over a part of the area. They were cut to a diameter limit, probably 24", and for a restricted number of species. They have remained untouched since then.

There are 25 stands or parts of stands in the watershed (approximate boundary) and they range in size from 1.3 to 184.4 ha, averaging 48 ha. They range in age from 89-186 years, averaging 138 years. The age refers to the mean age of the overstory.

No soil surveys have been done yet in the area; however for the site class distribution, the slope and soil depth are very important; probably related to 1/depth of soils and position on the slope.

Another dimension of site classification (above was site quality i.e. ht/age) is to classify site types by lesser vegetation. The ground vegetation here is typical of this forest type with a leaf litter layer and low young maple seedlings.

The soils of the area are typically Brunisols. The soils vary in:

a) surficial material which is ablative till, some minor fluvio-glacial deposits, some alluvian along the Batchawana, and some organic.

b) mineralogy (mixed, glaciers moved N to S).

c) depth - generally related to topography; shallow soils upslope, deeper soils downslope.

d) profile development, mostly brunisols evolving toward luvisols, but never quite making it because of the cold.

Currently, there is some small watershed work at Nippigon. Also, there was some work undertaken at Kirkwood from 1970-1973 looking at a stand of jackpine and at the change of precipitation chemistry as it passed through the forest itself. The throughfall chemical balance and soil profile were examined.

For tables on forest stands and site class distribution see Appendix Eighteen.

At the end of this presentation, the following questions were posed:

DAVID BALSILLIE: Is there any air monitoring in that area?

IAN MORRISON: No, but perhaps the A.E.S. will become involved. At the moment, we are only doing precipitation throughfall work.

LEN BARRIE: We plan to put a station there.

FRANK HICKS: If the timber is merchantable, you should have the M.N.R. classify it as a protection forest so your studies will not be interrupted.

IAN MORRISION: We have already approached the M.N.R. and they will protect it.

SAM LINZON: Are the tree ages of 130 years old growth?

IAN MORRISON: Yes, it is old growth. By 1980 the trees will range between 86-185 years, averaging 138 years.

SAM LINZON: Are the trees mature or over-mature? Have there been any growth studies?

IAN MORRISON: There have been some tree growth studies on primary production - litter production as a measure of actual production.

DAVE BALSILLIE: Are there any seedling plots of any type?

IAN MORRISON: Not really.

g) Lake Acidification Studies in Nova Scotia
- J. Kerekes

We are currently doing ion balances in two lake basins.

The lakes in the Atlantic Region are fairly similar. The major difference is the strong maritime influence of precipitation. The winter precipitation form is uncertain and a strong rain could cause the snow and ice to melt. As a result, we do not have the spring drop in pH. The ground is usually saturated at the beginning of winter.

The Department of Fisheries has recently been studying the decline and disappearance of Atlantic Salmon. For the fish hatcheries, the problem appeared to be with the actual river water due to a low pH. When the intake water was limed, the problem disappeared.

In addition to the Department of Fisheries work, the Province of Nova Scotia has set up precipitation monitoring stations as well as CANSAP. The province is also surveying lakes in Nova Scotia. In Newfoundland, the Department of Fisheries is surveying the lakes.

Most of the area in the Maritimes is susceptible since it is composed of granite rock and slate with only a few exceptions. (One exception is Prince Edward Island).

The study sites (three lake basins) lie in the boundary of Kejimkujik National Park. Some previous data exists on these lakes. They are very dilute with a low pH and have a salinity of 10 mg/l. It is a sensitive as well as a

protected site. The site is the maximum distance from the sea and from Halifax and Sydney as possible which constitute the only local sources.

The site area is approximately 150 square miles. We are studying two headwater lakes; they are very clear and contain no sphagnum. Lake Kejimkujik, which has already been gauged, is an important large lake. Beaverskin Lake and Lake Pebbleloggitch are side by side. Lake Pebbleloggitch exhibits a strong humid influence. Kejimkujik Park is in a flat area that is not pure bedrock as there is some glacial debris. The lakes in this area are very shallow. Na and Cl are the major ions with a very low concentration of Ca. In Lake Kejimkujik the H^+ ion surpasses the K^- ion and it has more ions in total.

The annual mean precipitation in the area is 1,200 ml. or 84 cm and the runoff is 71 cm.

In 1978 the annual weighted mean pH of precipitation was 4.6 with a monthly mean ranging from 4.2-5.1. The pH of individual events varied from 3.5 to 6.4. The pH of the clearwater lakes is lower during the wet years. The humid lake had the lowest pH of 4.1 to 4.5.

The range of pH can perhaps be attributed to the closeness of Halifax. We do have historical data for Morsey River, since 1954. The pH levels at that time were 5.5 to 6.5. This value dropped to 5.0 by 1965 and again to 4.8 to 5.0 by 1978.

All three lakes support fish but the humid lake, Pebbleloggitch, only contains stunted yellow perch, brown bullhead and American eel.

For maps of the area and more extended data, please refer to Appendix Nineteen.

After the presentation, the following discussion occurred:

JACK DONNAN: Are there any susceptible areas in Maine since it is close to the border of Nova Scotia?

JOE KEREKES: Yes. Acidic precipitation in Maine is recognized as a problem.

HANK RIETVELD: For the sites away from Halifax, are the wind patterns from the United States?

JOE KEREKES: The wind is from the U.S.A. and long range transport seems to be the cause of the problem. For areas near Halifax, the problem can be attributed to the smoke stacks of Halifax. In a study undertaken by Gorham the pH dropped considerably in the locality of Halifax.

h) Aluminum Controls - A Preliminary Model
- J. Kramer

For a detailed description of Dr. Kramer's presentation, please refer to Appendix Twenty .

After Dr. Kramer's presentation was completed, the following discussion ensued:

NELS CONROY: If the ratio of iron to aluminum (Fe/Al) is 1:1 as M.O.E. numbers purport, what would iron do to surfaces relative to aluminum and silicon?

JIM KRAMER: It would look a lot like aluminum. However, there is a compensating effect where amorphous iron in a solution of pH 7.0 would have no effect; but in a solution of pH less than 7.0, it would contribute to the effect of aluminum.

The more iron, the greater the iron compound. Therefore, in an acid lake, iron tends to neutralize the surface and aluminum is in lower quantities.

NELS CONROY: In caged limestone substrates of low particle size, there are high precipitates of aluminum on the surface of the filter papers and low precipitates of iron; however, silica is ignored.

PETER DILLON: In particulate kinetics, two filter papers are needed one on top of another. Could there be a problem with the filter papers?

JIM KRAMER: It is possible; however, the filters are washed with nitric acid which helps reduce contamination of this kind. The added iron may be due to surface reactions.

PETER DILLON: In the case of particulates, the problem becomes worse when the filters are washed with nitric acid.

JIM KRAMER: The surface reaction aspect should be more fully investigated.

BARRY LOESCHER: Perhaps there is a difference between laboratory filtration and field filtration.

JIM KRAMER: There are a similar number of dangers in the field and in the laboratory.

BARRY LOESCHER: It's easy to pick up aluminum contamination in the laboratory, but not so easy to pick up a loss.

JIM KRAMER: There is a loss in the polypropene with both methods. Some samples are higher and some are lower, from pH 7 down to 5 when they should have been within a few percent.

BARRY LOESCHER: You lose a lot of precision with standard additions.

JIM KRAMER: Also, manganese has a tremendous interference aspect.

LEN BARRIE: Why is there all this concern about aluminum?

JIM KRAMER: Aluminum is a well-known toxin to terrestrial plants. Carl Schofield in his experiments in the Adirondacks using the colorimetric method analyzed his samples and obtained results of levels from 400 to 500 ppb. When he went back to the lab and added aluminum salt, the fish died; however, when he added citrate, the fish did not die as it is a chelator of aluminum.

LEN BARRIE: Were the pH levels toxic?

JIM KRAMER: The pH itself is not the concern, but rather the fact that low pH can drive aluminum back into solution.

LOU SHENFELD: Then aluminum is toxic to fish.

JIM KRAMER: So they say at Hubbard Brook, but our experiments seem to show otherwise.

GREGG VAN VOLKENBURGH: Have you travelled to the Adirondacks to measure their samples and, at the levels that they measured, when the same amount of aluminum salt was added, was the solution then toxic to fish?

JIM KRAMER: Not yet, but we only have preliminary results at the moment. However, I don't think we have a storage problem with aluminum.

i) Alkalinity Deficiency as an Index of Acidification - M. Thompson

Mary Thompson is currently engaged in studies of surface water chemistry to demonstrate the effects of acidic precipitation on the chemistry of this micro-regime.

Figure 1 of Appendix Twenty-One is a copy of Henriksen's line diagram of pH versus Ca, with an empirical line to illustrate lakes that received acid rain and those that did not. Figure 2 lists the equations used to obtain the emperical line. This line was then put into a log function. In a semi-log plot of Ca vs pH using water chemistry data from the Labrador Lakes in the Churchill River System, instead of a curve to separate the lakes, the lakes followed the line. The line of slope is 1:1.

Surface water pH and bottom pH vary and the pH is higher in the summer and lower in the winter. (Assume CO_2 pressure of 10^{-2} atm.) Also, a softwater lake is limited in nutrients and algae constitue a mechanism to convey CO_2.

When we tried mock data sets and played with Ca/bicarbonate ratios, there was a constant ratio between calcium and bicarbonate (1:1 slope). By reducing the amount of bicarbonate, (deducting from each point the same amount of equivalence) we generated a curve. From this curve, we deduced that there is chemical erosion of an acid nature before carbonic acid weathering since pH's can vary over one pH unit.

Then we looked at alkalinity and calcium directly:

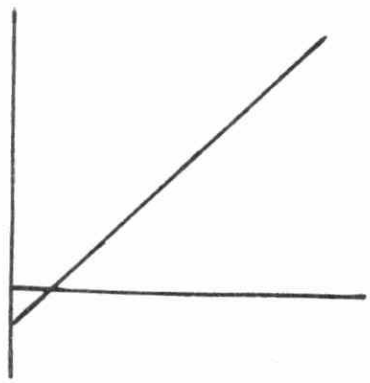
$$H_2O + CO_2 \longrightarrow H^+ + HCO_3$$

The more alkalinity is destroyed, the steeper the slope becomes. Figure 3 depicts an alkalinity - calcium regression curve for the Labrador Lakes. There is a negative intercept; the amount of missing alkalinity is related to the acid load in the area.

Figure 4 of Appendix Twenty-One is a pH vs Ca graph for Nova Scotia lakes near Halifax (1955-1977). Most lakes surveyed show increases in Ca; i.e. they were disturbed by constant activity. Undisturbed lakes show a drop in pH and Ca remains the same.

Since basins and lakes supply cations or alkalinity at a certain rate and the atmosphere supplies acid at a certain rate, we should be able to determine the rate of acidification. To determine the cation denudation rate, we obtain the mean cation concentration of a river at the mouth. Once we know the discharge rate and the concentration, we can calculate the cation denudation rate which is compared to the H^+ loading rate in the same units.

In an alkalinity vs Ca graph of New Brunswick creeks sampled for one year, there was a strong correlation as well as a negative intercept.



Since the Ca concentration varies from 1-6 mg/yr., then the H^+ input must be constant all year to show linear data sets.

Another example, that of the Mississagi River at Mississagi Chute, is illustrated in Figure 6 of Appendix Twenty-One. This River is receiving acid at a rate of one third of the calcium denudation rate. Figure 7 is a comparison of atmospheric loading rates of H^+ with the cation denudation rates of the drainage basins.

In order to determine the rate of acidification, we have to choose a basin or set of lakes with a cation denudation rate near the H^+ loading rate.

After Mary Thompson's presentation was completed, the following discussion occurred:

HAROLD HARVEY: How do you know when the cation denudation rate is near the H^+ loading rate? From monitoring stations where acid loading is in meq/m^2, the H^+ loading varies

from year to year.

MARY THOMPSON: The cation denudation rate is calculated from the river chemistry and can be marginally higher than the loading rate.

JIM KRAMER: With respect to your rate plots and deviation, would you obtain the same results if the weathering was done through $CaSO_4$?

MARY THOMPSON: As long as the calcium to bicarbonate ratio remains the same, you would still obtain a one to one relationship. If the ratio changes, there is a strong correlation.

JIM KRAMER: Is it possible to generate a change in the ratio if you had removal of $CaSO_4$ from rock by acid weathering?

MARY THOMPSON: We used mock data sets and discovered that if you have a constant ratio of calcium to bicarbonate, the linear relationship remains the same.

LEN BARRIE: Are there no other sinks for calcium to disturb the ratios?

MARY THOMPSON: Electrical neutrality must be obtained in the watershed. In precipitation chemistry, sulphate is only two thirds of the acid loading and nitrate constitutes the rest. However, nitrate does not stay in the water. We started by looking at what acid rain has done to the bicarbonate in the water.

PETER DILLON: It is important to remember that the output may only be part of the

cation denudation rate. In Hubbard Brook studies the runoff constituted one half of the degradation rate; you must measure the accumulation in the biota.

MARY THOMPSON: We assumed a steady state on an annual basis.

PETER DILLON: The state would not be steady over one year; you would need approximately 100 years.

MARY THOMPSON: We had 13 years of data for Nova Scotia and obtained a relatively linear relationship. The cation denudation rate was 52 meq/m^2 with a standard deviation of 9. There was not much evidence of change in the rate, just a suggestion of a slight decrease.

HAROLD HARVEY: Yes, but the biological pool can be easily underestimated. For example, there is a strong reservoir of iodine in the thymus gland of fish.

LAURA JOHNSON: In our considerations of sinks and pathways of precipitation to lakes, we have totally neglected the effects of groundwater on the system. An important input to chemical changes is being ignored: the effects of over-burden on water as it percolates through.

MARY THOMPSON: For the Mississagi River, can we assume in winter that it is ground water?

NELS CONROY: The surface water flow is controlled by the watershed. Ground water input may vary from zero to a great amount.

LAURA JOHNSON: There is a distinct seasonal variation of ground water, even in deep ground waters.

NELS CONROY: In the Killarney area, there is a change of 1 pH unit in the stream during the summer, but the pH remains constant in the spring when most of the runoff occurs.

LAURA JOHNSON: Perhaps there is unseen ground water input through the lake bottoms.

NELS CONROY: If that is true, it would be very important to the fisheries people who have selected a microenvironment for the fish to utilize during a critical stage of their life.

3. Open Discussion

H. Harvey, as session chairman, summarized the key issues of this session for open discussion. The needs for this area are the following:

1. Long term monitoring of the rates of acid loading and its effects on soils as well as a short term effects study to give lead time to the long term study for forest changes.

2. More consistent soil classification.

3. Fine scale mapping with a view to relating surficial geology to water chemistry of streams and lakes.

4. Understanding of the effects of low pH on lake trout and brook trout in their natural environment since approximately

2,000 lake trout lakes are in the major susceptible area.

5. Better lake names.

6. Three tiers of approach to alkalinity/ pH surveys:
   a) M.N.R. - broad survey
   b) M.O.E. - intensive survey
   c) Various agencies - intermediate

7. Further research into the aluminum toxicity problem.

8. Better understanding of the calcium bicarbonate relationship.

9. Ground water input monitoring.

10. Contribution to acid loading by humic material.

After the above points were listed, the following discussion occurred:

JIM KRAMER: In the acidification of dystrophic lakes, alkalinity may be contributed to from humic material. The substance has a higher dissociation constant at a pK of 4. The H^+ ion would be too high and enough bicarbonate could not be set into solution at lower levels of H^+ ions. Eighty per cent of the buffering capacity is not calcium bicarbonate.

MURRAY JOHNSON: Biologically, low alkalinity lakes that are dystrophic fall into different categories than oligotrophic.

NELS CONROY: We have to re-define a 'dystrophic' lake. There is no set of parameters for a dystrophic lake.

MURRAY JOHNSON: Oligotrophic lakes are very efficient in recycling nutrients whereas dystrophic lakes are very tight sinks, and mineralization at low pH is impaired.

Most studies focus on direct effects on organisms such as fish and ignore the overall economy of the lake system. A slowing down of the productive capacity of lakes is rarely studied; however, small amounts of pressure in such areas can remove fish after several years.

PETER DILLON: It is evident that fine scale geochemistry is very critical to soft water lakes. However, we cannot map 150,000 lakes. By remote sensing of the area, we can determine the susceptibility of the area. For fine scale mapping we need the assistance of terrestrial people.

FLOYD ELDER: What criteria do we use for remote sensors?

PETER DILLON: These areas will have to be calibrated with mapped watersheds.

NELS CONROY: Remote sensing is a difficult approach since the geological work would be impossible. The depletion of H^+ ions in upper layers of the soils would not be reflective of lake systems. The alkalinity may come from lower layers.

JIM KRAMER: In a study of two lakes north of Sudbury in a heavily impacted area, we discovered a tremendous difference between two lakes although they were only 300 m apart. Shoefly Lake was a hard water calcareous lake with a pH of 8.0 and an alkalinity of 2.5. There was no surface input or output. The other lake was a surficial drainage lake with a pH of 4.2. The lower layers of Shoefly Lake were intersecting with calcium carbonate materials whereas in the other lake we drilled down to 10 m. and there was not a sign of calcium carbonate.

4. Session Recommendations

1. Take immediate steps to ensure better integration of the aquatic and terrestrial effects studies.

2. Begin as soon as possible a major long term soils and vegetation study on a provincial scale.

   (i) Resolve the problem of differences of U.S./ Canada soil classification schemes.

3. Establish a major program to obtain good alkalinity and pH data for as many of Ontario's lakes as possible.

4. Take the necessary steps to standardize, as soon as possible, mass balance budget methodologies as they apply to calibrated watershed studies.

5. Begin a major program to define in detail the relationship between alkalinity and associated watershed geology.

6. Focus efforts on discovering and delineating in great detail the physiology of the toxicity of Hg, Al, and Pb on aquatic ecosystems.

D. SESSION 4 - Socio-Economic Aspects of the LRTAP Problem

1. Session Introduction - M. Johnson

There is a parallel between the activities concerning the Great Lakes problem and the Long Range Transport of Air Pollutants problem. Since the International Joint commission for the Great Lakes has been functioning for several years, we can learn from the Great Lakes experience and avoid several pitfalls.

The similarities are as follows:

a) In the course of implementing pollution abatement strategies, an interim strategy was employed whereby the pollutants were moved from the near to the far field and the consequences of this move are catching up.

b) In both cases, there is the tendency to deal with one pollutant at a time. This type of tunnel vision is illustrated by the way phosphorus was treated in the Great Lakes whereby the heavy metal content of sludges increased due to phosphorus precipitation. A balance was finally achieved between landfills and incineration.

c) The approach in both cases is founded in engineering and science and we are caught short by the energy crunch. We are arguing for remedial measures in tons or ppm and the counter argument is in dollars. Therefore, we are not

dealing in the same currency. The resources on the Great Lakes do have value: drinking water, recreational aspects.

The compelling arguments in human health terms must also be heeded and they might be of tremendous consequence to Ontario regarding the LRTAP problem.

d) In the Great Lakes study, no reasonable assessment of the Canadian and American publics' wants were undertaken. The goals used by the IJC almost totally ignored the social aspects and they should really have been of the most importance. Still, it is difficult to assess society's wishes for they often seem at variance. For example, in general, Sudbury residents are opposed to liming to combat the effects of acid precipitation whereas Muskoka-Haliburton residents are totally in favour of liming as a solution.

As regards the LRTAP problem, the dimensions are large. Authority divisions and responsibility arguments between Ontario and Canada, Ontario and Quebec, and Canada and the United States can be foreseen. The people in fisheries tend to narrow the argument, but it is not possible to limit the parameters; other values besides the dollar value of fish catches are needed. We need broad based arguments with long-term appeal. In undertaking such a socio-economic study, we must be careful.

2. Presentations

a) The Economic Implications of Acid Precipitation
- J. Donnan

For a detailed outline of Dr. Donnan's paper, please see Appendix Twenty-Two. Besides the information available in the Appendix, Dr. Donnan also delivered the following material:

Implications on Distribution

The LRTAP problem is plagued by the distribution of the various sources in relation to the cost of controls and the measurement of damages. Incentives for the different parties to act, specifically for control costs, are needed. For example, if to solve the problem, most of the control costs will be borne by the U.S. and most of the damage costs by Canada, we will have to enter the bargaining arena with other tradeoffs such as energy.

Control Strategies

A. Dispersion - This strategy was essentially the source of the problem.

B. Emission Reduction
   1. which sources should be reduced?
   2. how much at each source?

C. Remedial Activities
   1. lakes and waterbodies - liming
   2. breeding of acid resistant fish

D. Implementation Incentives - Incentives will be needed to induce people and companies to do something that they do not wish to do.

E. Compensation for damages.

All the above strategies are not mutually exclusive.

Information Requirements for Strategy Development

1. Current levels of ecological effects. Emphasize magnitudes and aggregations.

2. Relative importance of effects, i.e. economic and social consequences, through surveys of attitudes and preferences.

3. Distribution of sources and causes.

4. Distribution of damages.

5. Control strategies scenarios, i.e. technical feasibility of mixes and methods and costs of specific levels of control.

6. Predictions of consequences of strategies

   a. changes in precipitation acidity

   b. changes in acidity of watersheds

   c. reduction of damages or elimination of problems - ecological
      - economic

d. people's perception of this problem.

7. References from people for anything where dollar values have been associated with acid rain.

8. Lake surveys; possibility of collecting other data such as the use of waterbodies, accessibility to waterbodies, fish life, development on waterbodies including cottages, marinas, resorts, etc., use of drinking water, angling success, recreation, boating, any other unique features.

3. Open Discussion

M. Johnson, as session chairman, outlined the key issues for discussion raised by Dr. Donnan's presentation.

1. socio-economic approaches

2. LRTAP issues

3. societal goals

4. remedial strategies

5. political considerations

6. information needs

Discussion of the above points then ensued:

HAROLD HARVEY: The OFIS data base contains information on 6,000 to 7,000 lakes. However, it may not give you angling success.

JACK DONNAN: Does this data base correspond to the acid precipitation study?

HAROLD HARVEY: Some of the work does.

MURRAY JOHNSON: When Ontario maintained resident angling licenses, a data base was established. Perhaps it could be interfaced with a lake inventory.

HAROLD HARVEY: In Michigan, the number of anglers fell by one-half when the license cost $1.00.

GREGG VAN VOLKENBURG: One of the things we learned from the times we spent in the field at Nanticoke was that people's fears seemed to centre around the health effects.

JACK DONNAN: My list of important damages includes health effects.

CAL WARDEN: Other issues including visibility and deterioration are involved when one discusses LRTAP as opposed to only acid rain.

FLOYD ELDER: The way we perceive the issue is not the same as the actual economic and social concerns due to the decreased usage of water.

GREGG VAN VOLKENBURGH: The education of the public is of paramount importance. We should explain the legitimate scientific concerns and then wait for feedback from the people on their concerns.

HAROLD HARVEY: In many areas, people feel that there was no pollution eight years ago before we scientists appeared on the scene. This misconception has been fed through to the political level.

GREGG VAN VOLKENBURGH: We still have to answer the public's concerns.

KEN TRENT: When using scenarios, we assume we know how to solve the problem.

JACK DONNAN: The idea behind the use of scenarios is to pose various solutions and through the use of models, to determine the effects of these solutions. The issue revolves around the uncertainty of the consequences of the scenarios.

LOU SHENFELD: Where will you obtain the dollar value loss to the sport fishing industry in Ontario?

JACK DONNAN: With the help of the M.N.R.

JOHN ALLIN: We have carried out some household surveys. Our basic data is from our 1970 survey but we did a small follow-up survey in 1975. We also did another survey in 1978. From the number of angler days, we determined that the expenditure in the province for sports fishing in 1972 was $215M and in 1979 $600M.

CAL WARDEN: Was the Ministry of Industry and Tourism involved in these surveys?

JOHN ALLIN: No.

MIKE POWELL: There was also a study done on Lake Nipissing and a report is available on the value of the Lake Nipissing fishery.

PETER DILLON: The Ministry of Housing has a data set available on the socio-economic

impact on lakes in the Muskoka-Haliburton area through the Lakeshore Capacity Study which has been ongoing for five years. There is a broader range of data available than just chemical and biological data.

JACK DONNAN: What about correlating this data with the chemical data?

MIKE POWELL: There are still a number of variables to consider. We will mail you a copy of the survey. When, for example, 10 lakes are fished out, tourists just tend to move on to other lakes.

MURRAY JOHNSON: It is difficult to determine if lakes were exploited by fishermen or the fishery ruined by pollution. For example, in Lake Superior, the fishermen depleted the stock.

JACK DONNAN: We will first attempt to compile physical damages and losses before assigning dollar values to them.

CAL WARDEN: Do you plan to look at damage to structures and buildings as well? There is data available.

FLOYD ELDER: It might be difficult to assess if the damage is due to local effects or LRTAP.

LOU SHENFELD: Air pollution combined with humidity has caused more corrosion problems than acid rain.

GREGG VAN VOLKENBURGH: The European experience was that aluminum siding corrosion was aggravated by the presence of the $SO_4^{=}$ aerosol.

LOU SHENFELD: That's not acidic precipitation.

JACK DONNAN: I'm getting confused. What is the difference?

LOU SHENFELD: The overall problem is the long-range transport of air pollutants with acid precipitation as one part of it.

JACK DONNAN: In order to resolve the acidic precipitation problem, we must discriminate as to what causes the actual damages.

GORD McBEAN: For a more rational strategy, you have to look at the whole LRTAP problem.

GREGG VAN VOLKENBURGH: Control of LRTAP will affect various areas. The bargaining starts with the federal government and we will need data to support our statement on damages.

LOU SHENFELD: I hope we are more successful than continental Europe was with the United Kingdom.

JACK DONNAN: We can use energy tradeoffs.

ED PICHE: We cannot forget the urgency of the issue. We are working within a restricted timeframe which puts constraints on our studies. Negotiations between Canada and the U.S. may begin soon and we will not have all the technical information that we need.

MURRAY JOHNSON: The Boundary Waters Air Treaty was not developed overnight. I think we should refer this matter to the IJC under

the Boundary Waters Treaty for an opportunity to place all our information on the table for open discussion. The scientists are still entitled to their own opinion on various strategies.

GORD McBEAN: The Canadian and U.S. governments have been discussing the issue informally for the past two years. At the Washington meeting last December, the Bilateral Research Consultation Group was set up and the principles were drawn up by both sides. Then, the summer meeting was a more formal stage of discussion and we perceived a hardening of attitudes on the U.S. side because of Canadian pressure. The expectations of Canada and the U.S. agreeing, even on the principles of the BRCG are important. For the people negotiating the treaty, it is not possible, to go through the IJC. We also have Federal/ Provincial negotiations to undertake. The first step has been the establishment of a Federal/Provincial Control Strategies Committee.

MURRAY JOHNSON: We now find ourselves in an awkward spot since the governments have segregated the air quality and water quality groups. It was not in our best interests to compartmentalize as it leads to rivalries.

FLOYD ELDER: Even if it were economically **feasible** to find alternative occupations for those people involved in the fisheries industry, we are still faced with the argument that people have an inherent right to fish if they wish. The avenue to show that right may not be through dollars and cents.

GORD McBean: We are poorly advised to argue with the U.S. on the basis of costs. We should perhaps argue on idealized principles. Take the analogy that the Americans are very upset about oil spills and not just from the point of view of their dollar value.

MURRAY JOHNSON: The U.S. has similar acid precipitation problems in the Adirondacks.

ED PICHE: Jack, what is your timeframe for a final document on the socio-economic effects?

JACK DONNAN: During the winter, we will be engaged in assembling the data and establishing correlations between parameters as well as considering the best methodology to present the data. In the spring of 1980, we will be ready to do further surveys if necessary. By January 1981, we should have a tentative policy document and by the fall of 1981, we will be discussing strategies and consequences. Canada needs a position stating what it wants, and what it is willing to forfeit to achieve those ends.

GORD McBEAN: We still need to know the numbers involved.

TOM BRYDGES: Is there any action on the federal level to obtain socio-economic aspects in the other provinces?

FLOYD ELDER: We are currently looking at the sensitivity of areas, but not the socio-economic aspects. Still, it should be easier to quantify the effects on commercial salmon fisheries.

TOM BRYDGES: Are the other provinces more dependent on tourism?

JACK DONNAN: We have a Task Force set up to study the problem.

JOHN ALLIN: What is your budget?

JACK DONNAN: We have applied for funds as part of A.P.I.O.S. Total Funding. Dr. Munn of the University of Toronto applied to the federal government for funds to do socio-economic studies. Also, I think the federal government has published a report on a study of the economic loss in forest growth.

FLOYD ELDER: The damage to the forest ecosystem is very subtle.

JACK DONNAN: Is there a possibility of additional efforts in the socio-economic area even if Munn's proposal is not accepted?

GORD McBEAN: Yes.

HAROLD HARVEY: We are overlooking one important aspect; there is no clearinghouse to store all studies going on. If we had such a clearinghouse, we would avoid duplication of studies. If you wanted to know what the fishery was worth in OLA Lake, I could give you the dollar value in half an hour. Unlike the Swedish effort, we need to be well-coordinated and receive feedback as to whether or not we are on course.

GORD McBEAN: We are undergoing a full program review at the senior management level to determine whether or not our current activities will meet our needs.

ED PICHE: As a result of the A.P.I.O.S. objectives, the Socio-Economic Impact Committee was established.

HAROLD HARVEY: As of this point in time, there is no proof that acid rain is causing a loss of fisheries. We need documentation.

LOU SHENFELD: If you take that a step further, then there is no proof that INCO's emissions are causing acid rain.

HAROLD HARVEY: There are five stages from when the material goes up the stack until the effects are seen. A more integrated study is needed.

FLOYD ELDER: Take the example of Lake Erie. It could not be decided if its 'death' was caused by phosphorus or carbon, but the agreements for control were reached before the causes were established.

4. Session Recommendations

1. It is imperative that a central clearinghouse be established for all activities relating to the L.R.T.A.P. and A.P.I.O.S. programs. This should be set up through the coordinators of the various programs.

2. It is imperative that all study teams, both Federal and Provincial, be vertically integrated, i.e. terrestrial and aquatic effects study teams should not be separated.

3. It is advisable that all efforts not be focussed on just one aspect of the problem of the long range transport of air pollutants. Rather, all agencies should support a "holistic" approach to this issue.

4. It is imperative that the socio-economic activities not be disjunct from the scientific activities.

5. It is very important that any and all socio-economic arguments that are going to be utilized when dealing at the international level are broad-based with long term appeal; that is, short term or interim only solutions should be avoided.

E. SESSION 5 - Remedial Measures

1. Session Introduction - T. Brydges

The following comments pertain to liming of lakes, since it is the only viable remedial measure that is currently available.

Even though abatement is the ideal long-term solution, will it arrive in time to save our lakes? It is reasonable to assume that Ontario will lose fish in important lakes. Therefore, we need a remedial methodology such as liming or neutralization in the interim.

Priorities

1. Sport fisheries

   Under this category, there are four possible scenarios:

   a. no liming needed, only a modification of current management practises.

   b. liming plus restrictions on usage.

   c. lime lakes where resorts are located for economic viability.

   d. write off lakes as cottagers there are satisfied.

2. Ecologically important fisheries

3. Human health considerations

This aspect will increase in importance in the future, i.e. drinking water.

4. Political pressures

The next area to consider is problems with liming. The problems listed below will probably surface with all interim mitigative methodologies.

1. The method must be cost effective. Fish productivity must increase as a result. We also must consider who will pay for the liming.

2. The method must be safe. Will there be any side effects, long term changes, or accumulation of other materials? Plus, how long will the effects last?

3. We must consider the long-term maintenance aspect. If cottagers' associations begin to lime lakes, who accepts the liability? Who will control the liming, will it come under the Fisheries Act or the Environmental Assessments Act?

4. We must also look at the management of the fisheries when liming is completed. For example, if a Cottagers' Association limes a lake at its own expense and the fisheries improve, there is always the possibility that others will deplete the stock. In Sweden a "user pays system" has been implemented. If a lake has been limed, a fisherman must pay money to be on that lake.

At this point, let us look at what is still needed before the implementation of an interim mitigative methodology such as liming.

1. We still need a strategy agreement within Ministries and between the two governments involved. Will we take the remedial route? If we do, to what limits, will we lime? We do not wish to be stampeded into liming lakes by Cottagers' Associations and politicians.

2. We still need technology development in the area of liming and fish management.

From the points that have been raised above, you can see that we have a large area to look at in the future, if we decide to follow the liming route.

2. Presentations

a) Findings from an in situ experiment using limestone to enhance the hatching success of rainbow trout (salmo gairdneri) eggs in an acid lake. - J. Gunn

For a detailed outline of J. Gunn's paper, refer to Appendix Twenty-Three.

In conclusion, Mr. Gunn stated that we need to attempt various stocking efforts with larger fish, different species of fish and at different times of the year.

After Mr. Gunn completed his presentation, the following discussion ensued:

LOU SHENFELD: How does the use of lime compare to the use of rotenone?

JOHN GUNN: The addition of rotenone kills all fish in the lake, whereas the addition of lime essentially changes the dominance in the lake. The forage species will bounce back quickly.

JACK DONNAN: Will sports angling be sufficient to keep the forage fish under control?

JOHN GUNN: The perch would be too small for anglers.

LEN BARRIE: Why?

JOHN GUNN: They stunt themselves out through a rapid increase in numbers.

JIM KRAMER: Was there any evidence that the perch were taking over from the bass?

JOHN GUNN: The perch were very small sized.

TOM BRYDGES: What is the water quality in Joe Lake?

JOHN GUNN: It is improving.

DAVE BALSILLIE: What about stocking pike into a susceptible lake? Pike are a semi-acceptable sports fish.

JOHN GUNN: Susceptible lakes do not constitute a suitable habitat for pike.

MURRAY JOHNSON: Do you have any data on contaminants in the study lakes?

JOHN GUNN: No.

MURRAY JOHNSON: Isn't metal uptake enhanced in acidic lakes, i.e. mercury?

JOHN GUNN: We only discovered one lake with warning signs of increased mercury uptake.

MIKE POWELL: Since the experimental stock came from the same year class and the same hatchery, any increase in mercury uptake would be easy to detect.

NELS CONROY: Increased mercury uptake in acidified waters is only evident in laboratory experiments.

TOM BRYDGES: In field experiments at Burlington, it was concluded that when the pH goes down, mercury in the young of the year fish goes up.

NELS CONROY: In Swedish experiments, when only selected parts of a lake were limed, the fish seemed to be attracted to that part. The perch appeared stunted with high mercury content. Once the lake was limed, the growth of pike increased and the mercury content decreased.

b) M.O.E. Experience of Remedial Efforts in the Sudbury Area - B. Keller

Since little work has been carried out in the area of neutralization of stream systems, we decided to undertake such an experiment.

First of all, we studied potential sites and available literature in this area. We found a fairly good article on stream liming by Pearson and McDonnell in acid mining areas. They outlined a methodology for designing a limestone barrier for specific stream flows. They also devised a model for predicting the quantity of limestone needed whereby you just have to plug in the stream's characteristics. When we plugged in the information for our proposed site, we were astounded by the quantity of material needed. It appears that for acid mining areas, there is a heavy metal contamination problem which reduces the limestone's ability to neutralize. As a result, approximately five times as much limestone is needed. Due to the large quantities involved, we decided to reject our original proposed sites and look for a small creek that met our needs.

We finally decided upon Chikanishing Creek. There were some drawbacks to this selection, but it had the best advantages. The flow is essentially constant on an annual basis; during peak flow, it is only 10 cfs. Chikanishing Creek originates in a marshy area but there is no saltwater problem. There is a fairly diverse minnow species and fauna. We planned to use these organisms as monitors.

The searching week began March 15. During the spring runoff period, the pH decreased to 5.0 which is low enough to have some effects, perhaps on fish hatching experiments. In March the conductivity was 30 - 35, a very dilute system. Over

the course of the summer, the pH increased to 6.5 and the productivity tripled. The runoff was then largely groundwater.

To begin with, we calculated the amount of limestone needed using the following equation:

$$W = L_p \; Q \; D$$

where

W = quantity of limestone

L = load factor which is derived by laboratory studies and observing barriers in operation. The load factor strongly affects the solubility of the limestone.

p = per cent magnesium in limestone

Q = discharge flow

D = diameter of particle size. For a quickly flowing system, you have to ensure that the particle size chosen will stay put.

Since the minimum pH of Chikanishing Creek is 5.0 and we wanted to maintain it at 6.5, we calculated that we would need 350 tons of limestone.

L = 70 (derived factor from nomogram; length = 100 m.; depth = 2 ft.

p = 1%

Q = 10

D = .5

There were some practical constraints that came to light during the actual experiment. We were limited to where we could erect the limestone barrier since only a portion of the creek was accessible along the road. Therefore, we just dumped the limestone into the streambed which led to problems with siltation. We should have used 30 tons of larger diameter particles to prevent loss due to flooding. The total manpower required to do the job was 350 man hours.

At the end of Mr. Keller's presentation, the following discussion took place:

IAN MORRISON: What was the total cost of the operation?

BILL KELLER: 350 man hours at $5.00/hr. equals $1,700.00. The cost of the limestone and transportation was approximately $5,300.00. Thus, the total cost was $7,000.00.

LEN BARRIE: Imagine if you had to add helicopter costs. Do you think it will work?

BILL KELLER: We are hoping that we have overdesigned by a factor of five.

IAN MORRISON: What is the expected life of the barrier?

BILL KELLER: Close to ten years. There will be a period of barrier renovations since in order for the experiment to work, the barrier has to be gradually dissolving. The follow-up question to that is, how long will it work? We have no results

at this time since the stream character changes. We dumped the limestone in July and most of the barrier is not in contact with the water yet.

HANK RIETVELD: What if you stretch out the length and use a depth of one third?

BILL KELLER: We will have to wait until the results of this experiment are in before moderations are considered. Some chemical observations to date are:

- as the alkalinity goes up, the ambient pH was 6 - 6.5 but it has increased to 7.5.

- there has been a high deposition of iron (3 - 6 mg/l) downstream for 100 m. indicative of groundwater takeover.

- pH has increased and solubility decreased.

The deposition of iron downstream could be a potential difficulty.

HANK RIETVELD: Does the effect continue downstream?

BILL KELLER: The alkaline groundwater is diluting the effects. Upstream the alkalinity is 15 - 20, at the barrier, it is 40, and downstream it is 25. Still, there is no decrease in pH as you go further downstream.

3. Open Discussion

T. Brydges, as session chairman, made the statement,

"Remedial measures research is still in its infancy"; then encouraged comments.

LEN BARRIE: Has selective breeding been considered and researched as a remedial measure for sports fisheries?

JOHN GUNN: Not in Ontario, but there has been a program ongoing for several years at Cornell University with brook trout. In Norway, experiments are underway using brown trout. Still, there is a limit on how high you can push the tolerance levels. We have overemphasized the lower limits of sensitivity; effects already occur at a much higher pH. A pH of 6.0 can already pose a problem to fish species.

HANK RIETVELD: Are these effects evident at any particular age?

IAN MORRISON: Dr. Osborne at Lakehead University in Thunder Bay states that the effects are apparent at all age levels.

JACK DONNAN: Does this statement have any implications on the effort to provide an aritificial environment for hatching purposes?

JOHN GUNN: We are only halfway along in our experiments. We plan to continue with more tolerant species in the fall. In some calibrated watersheds, there are not very clean pulses. You can easily stock fry and fingerlings in lakes that have the same water quality, but eggs are cheaper. There is another advantage to a continuous habitat, and that is that fish in their natural habitat will reach a greater size than stocked fish.

JACK DONNAN: Can someone explain the issue of management problems for me? How can we have management problems when we have data on various lakes?

JOHN GUNN: Throughout the area, the lakes have been documented. There has been an expansion of coarse fish since they have a higher tolerance level to a decline in pH. This advantage in a chemically changing lake system is lost.

MIKE POWELL: The use of rotenone is not feasible on large lakes (100 acres) and lake trout lakes are usually large. Some other solutions are:

1. stock walleye in suitable habitats since they prey on perch.

2. stock larger perch.

3. stock lake trout at a larger size.

4. if there is a problem with perch in a brook trout lake, then perhaps rotenone could be used as brook trout generally inhabit small lakes.

LEN BARRIE: If 350 tons of lime do not come in contact with the water, would it be feasible to lime the soil in the area of a susceptible lake using forest fire aircraft?

TOM BRYDGES: A lot of limestone will be lost (approximately 50%) with most methods. You have to grossly overestimate the amount in order to account for spring runoff. One alternative is to dump the limestone on the ice every year.

MARY THOMPSON: The pH's measured on the Turkey Lake samples after aeration increased by 1 pH unit.

TOM BRYDGES: That's all right for a carbonic acid system but not for a mineral acid system.

BILL KELLER: There are different nomograms available.

GREGG VAN VOLKENBURGH: To dynamically add limestone to a water system, you would probably need a flow gauge and a level gauge which could monitor the amount dependent on streamflow.

BILL KELLER: The advantages of using fine material is that it is more reactive and creates a preliminary film. There was some information in the literature regarding the use of a well system but there wasn't enough documentation.

JOHN GUNN: Industrial slurry pumps might be a solution.

FLOYD ELDER: Is primary production lost with increased acidification?

PETER DILLON: We did not do any direct measurements of primary production but phytoplankton measurements in lakes in the Sudbury area showed an improvement. In a year, they were back to natural levels. For zooplankton it took from three to five years.

NELS CONROY: With a reduction in primary production, there is a corresponding simplification of the system. Diversity of life decreases.

TOM BRYDGES: The papers presented here have shown that the practical details of liming still need to be resolved. Now, let's look at the broader question of whether or not we go the reclamation route, i.e. abatement or nothing.

HANK RIETVELD: The abatement route will not be feasible in the next few years, so we cannot forget remedial measures. However, we must be careful that they are interim measures only and not regarded as a permanent solution to the problem.

MURRAY JOHNSON: Liming as an interim measure is our only recourse to save some genetic stocks of fish for later rehabilitation. Still, cost effectiveness studies may prohibit the use of liming in such a case; for example, even if damage has occurred, a hard economic analysis might not favour a rehabilitation program and cheaper methods may not produce adequate results.

LOU SHENFELD: What about letting the polluter pay?

TOM BRYDGES: The sports fisheries industry has economic value. Acid rain could be having an adverse effect on this industry resulting in a loss of money. Liming is a means for protecting these fisheries.

LOU SHENFELD: I still think the polluter should pay. We could take the Americans to court through their judicial systems.

TOM BRYDGES: From the societal point of view, if it will take $10,000.00 to subsidize a resort through liming operations, should the government pay or not?

HANK RIETVELD: Our waters are logistically important.

NELS CONROY: We still have to pursue research in remedial studies. Even if we bought all the available technology, it would take at least ten years before abatement would result in any significant changes.

HAROLD HARVEY: The inherent liability with the acid rain problem is that the impact site may be far removed from the emissions source. Take for example Norway and Sweden.

JACK DONNAN: We are confusing the issue. There are two separate questions here: efficiency and distribution. Let us say our objective is to preserve fisheries. Then, the efficiency question is, "What is the cheapest way of achieving this objective?" The distribution question is, "Who will pay for the means of achieving the objective?" The possible interrelations between these two questions can affect the actual condition.

HAROLD HARVEY: We cannot tell you how to maintain the environment in a pristine condition when we are being lashed by one gigantic insult.

JACK DONNAN: If one objective is not feasible, then we need another objective.

HAROLD HARVEY: Yes, but if we back off now, then we've lost our case. Any semblance of predictability is impossible after the system has been disturbed. The U.S. faced similar problems and established the Pristine Water Act for which objectives were set.

LOU SHENFELD: Objectives were set but in the courtroom nothing happened.

HANK RIETVELD: The ultimate solution might be a change in lifestyle.

JACK DONNAN: What are the implications for returning to a pristine environment in terms of technology and costs?

MURRAY JOHNSON: First of all, we would be obliged to describe what a pristine environment would be and any consequences apart from that. I personally object to the way this environmental game is being played by confrontation. We should be emphasizing planning in a holistic way with coordinated resource management to optimize benefits instead of by confrontation.

JIM KRAMER: There are two questions under discussion here. One is whether or not reclamation subsidies should be issued to maintain sports fisheries. The other is the need for a definition of pristine especially since natural processes are ongoing as well.

HAROLD HARVEY: I never suggested that we could attain a pristine condition in the environment. However, over the last ten years, waterbodies have developed until optimal relations in the waterbody were reached. Whatever we do, we would only make matters worse since it would be a further departure from these optimal relations. There would be enormous biomass changes, so I feel that we cannot solve the problem by sprinkling lime.

HANK RIETVELD: No one can argue with that statement. We may have to write off some lakes.

TOM BRYDGES: A major Ontario industry is either already or potentially in trouble. This fact will probably override the issue of acid rain. Even though abatement is still the major objective in the program, I think we should shift the research in remedial measures to a higher priority.

HAROLD HARVEY: I think we should put all our funds into abatement technology research.

LOU SHENFELD: That depends on our objective. Is it to maintain the sports fisheries?

GORD McBEAN: Sports fisheries are not a major concern. To maintain the environment is our major concern. Liming can be implemented as a remedial measure for the sports fisheries industry; however, for the environment, abatement at the source is the only solution.

FLOYD ELDER: I agree with the need for abatement. But, we lack evidence of what would happen when abatement is implemented. No models exist at the moment that can produce such results.

HAROLD HARVEY: There are several orders of magnitude difference between the LRTAP problem and other environmental problems such as PCB's.

FLOYD ELDER: We still need scientific models that can predict how control measures would affect certain ecosystems.

JIM KRAMER: Abatement is currently our technological limit. But, we have not even shown scientifically that if we go to the optimum level of abatement, our environment will be changed. We need predictive models and should pour our resources into this area.

TOM BRYDGES: Then, are remedial measures the avenue that we should pursue?

HAROLD HARVEY: What is the estimate of the cost of liming for South Central Ontario?

LOU SHENFELD: We have to evaluate the costs for accessible lakes.

TOM BRYDGES: The average cost is roughly 20K per lake. Therefore, liming on a large scale is not feasible technically or economically. Remedial measures should only be implemented on lakes of very high ecological value or for the protection of sport fisheries.

JACK DONNAN: What is our list of alternatives? We still need facts and figures of the actual number of lakes involved and then we should study alternative scenarios.

SAM LINZON: Our ultimate objective is still abatement. Liming is a possible interim preventative method and should be limited to very sensitive areas.

MIKE POWELL: You are assuming our success in achieving abatement. There will be at least 20 years of lag time once and if abatement is achieved. In the meantime, some lakes will die.

HAROLD HARVEY: Our supply of limestone is limited though.

MIKE POWELL: I'm not totally ruling out liming as a possible interim solution.

HAROLD HARVEY: A decision will have to be reached based on each individual lake.

GREGG VAN VOLKENBURGH: Our primary thrust should be to study the consequences of abatement. We better not emphasize liming as a solution. However, SO_2, SO_4, and N emissions will continue to increase.

FLOYD ELDER: Then you feel that research on remedial measures should be pursued?

GREGG VAN VOLKENBURGH: We should announce ongoing research in this area instead of completed experiments. Otherwise liming may be accepted as the ultimate solution.

FLOYD ELDER: What about putting money into the technology of sulphur movement?

GREGG VAN VOLKENBURGH: We should continue to monitor technological processes in such areas.

At this point, a consensus was reached by all participants that research in remedial measures should be pursued.

JIM KRAMER: There are other areas of study for reclamation. We should consider the potential for groundwater recharge for lakes. If high calcareous sediments are available in the area, then the potential is there to maintain a whole water system for many years.

4. Session Recommendations

1. It is absolutely essential that the following steps are taken in the following order:

   (i) Establish objectives.

   (ii) Determine the cheapest way to attain those objectives.

   (iii) Decide who will pay and how much.

2. It is necessary that the development of appropriate "interim remedial methodologies" continues with particular emphasis on whole watershed neutralization schemes. At the same time, it was agreed that the only acceptable long term solution is abatement at the source.

3. It is important that senior government management officials have all the relevant facts as they will be forced to make a policy decision on liming in the very near future. To this end:

   (i) Efforts should begin immediately to compile all experience on a world-wide scale.

   (ii) Continued experimental research in this field should be encouraged.

4. It is essential that every effort be made to encourage integration of socio-economic impact studies at all government levels. This integration should be handled through the Federal/Provincial Control Strategies Working Group and should be the responsibility of the program coordinators.

F. SESSION 6 - Future Directions

1. Session Introduction - F. Elder

This session is being held to help define future direction in terms of programs, future meetings, and the Ontario/Canada LRTAP Bilateral Research Consultation Group. This latter group was proposed by Mr. Drowley and Dr. Collin, but the terms of reference for the group have not been finalized yet.

This meeting itself has as its purpose to establish communications between the working scientists and the program management people. It was not a direct result of the BRCG. We wish to look at our accomplishments to date, and then discuss future meetings and what we wish to accomplish through them. Should there be any changes in the organization, structure, or the type of seminar?

So, to begin with, let us hear the future plans of the various organizations involved in LRTAP research.

2. Presentations

a) MOE Fiscal 1980/1981 LRTAP Program - E. Piche

The Acidic Precipitation in Ontario Study is an important program within the structure of the Ontario Ministry of the Environment and has received significant funding.

The areas of study have been priorized; however, the priority of tasks has not yet been approved by the Technical Committee. They have received tentative acceptance at the senior management level.

TASK # 1 Lake Sampling Program

To identify the number and location of susceptible lakes in Ontario. There is a three-pronged approach to this task:

Class #1 Lakes: Lakes sampled at least six or more times per year.

Class #2 Lakes: Lakes sampled from two to five times per year.

Class #3 Lakes: Lakes sampled once per year.

TASK #2 Deposition Monitoring Networks

To determine provincial acidic deposition isopleths. Some complications have arisen due to the extension of the Sudbury Environmental Study. We plan a network of approximately 30 Sangamo monthly samplers for next year, plus three concentrations of true event networks and support meteorology.

TASK #3 Intensive Aquatic Studies

The current plans are to continue the calibrated watershed studies at Dorset and Sudbury.

TASK #4 Socio-Economic Aspects

At this point in time, we are in the process of forming a Socio-Economic Impact Committee with representatives from the various Ministries involved. This committee will be responsible for all provincial cost/benefit studies.

TASK #5 Integrated Modelling Program

By integrated, we mean developing models that deal with all aspects of the problem, from source to receptor, including lakes and soils.

TASK #6 Data Bases Development

To establish a means of dealing with all information collected from our precipitation chemistry studies, our meteorology program, our socio-economic endeavors, and our lake susceptibility undertakings.

TASK #7 Intensive Terrestrial Studies

To catalogue susceptible soil and vegetative regimes in Ontario.

After Mr. Piche completed his outline of proposed tasks for A.P.I.O.S., the following discussion occurred:

DAVE BALSILLIE: What is the predicted longevity of the A.P.I.O.S. program?

ED PICHE: It was set up as a two phase program. The initial phase is a two-year commitment which ends in the Fiscal Year 1980/81. After Phase One is completed, a preliminary draft report outlining proposed avenues of action and the implications of the results is expected. Then, senior management will make a decision regarding Phase Two.

FLOYD ELDER: Does Task #5 "Modelling" only encompass atmospheric transport models?

ED PICHE: No, it is an integrated modelling program and lake budgeting is included as well as atmospheric transport modelling. The word "integrated" refers to a more universal scale study of the complete phenomenon: LRTAP, deposition, lake modelling.

LOU SHENFELD: Do you have another budget for remedial measures?

ED PICHE: Remedial measures are included under Task #3, Intensive Aquatic Studies. Task #1 will establish the susceptibility whereas Tasks #1 and #3 together will establish the timeframe involved. There is also a real possibility that remedial measures will be covered in another area. INCO has proposed major funding of research in remedial measures. Perhaps, they will be covered off by industrial and private agencies.

LOU SHENFELD: Do you mean the studies will be carried out by private researchers with Ontario government funding?

ED PICHE: No! I mean that they are covered under Task #3, not explicitly but implicitly. For example, Dr. Harvey's fish research is covered under Task #3.

GREGG VAN VOLKENBURGH: I would like to comment on the draft of the Fiscal 1980/81 budget. Could you incorporate a list of other activities related to this program but funded separately by the government?

DAVE BALSILLIE: Will the other activities of the branches and regions be piped into this, e.g. the regional monitoring programs?

ED PICHE: They are already incorporated into the draft budget document.

b) Federal DOE LRTAP Program - H. Martin

The federal program is supported by Environment Canada as well as by the Department of Oceans and Fisheries. This presentation deals with the research planned by Environment Canada.

Our research studies are carried out in all of Eastern Canada; east of Manitoba and including Ontario. There are four main sections of the program:

1. Inventory Studies - F. Vena

We have a rough sulphur inventory for anthropogenic sources and a natural sulphur inventory.

Our plans call for an update of SO_2, NO_x, and particulates for early 1980. The next step will be inventories for natural NO_x emissions, hydrocarbons and ammonia.

2. Atmospheric Modelling - E. Voldner and L. Barrie

You have already been introduced to the regional type model. The next step in this area is to increase future effort and funding as this type of model will provide scenarios of potential injury. However, it is wasteful to put models together independently, and we definitely need greater cooperation here.

Mr. Barrie has already described our $SO_4^=$ Precipitation Acidity Model. We will continue in this area, particularly in our examination of $SO_4^=/SO_2$ ratios.

3. Atmospheric Modelling - L. Barrie

L. Barrie has already described our experimental APN network. This network will be extended when our watershed study sites in Quebec and at Algoma, Ontario are finalized.

The CANSAP network will continue for approximately five to ten more years. There are currently 55 stations in this network. One problem that we envisage will be the changeover of Sangamos, as they will be out of production in two years. The cost of this switchover will be about $100 K. We are having problems with evaporation and leaky lids.

We also plan to continue our Great Lakes Basin Precipitation Network over the next few years.

There are several aspects of the atmospheric program which have been neglected to date.

a) The process of oxidation or transformation. This parameter is needed by the modellers but we are in no position to define the transformation processes with any clarity. As a result, we are attempting to do more in this area.

b) The accuracy of deposition velocities. These velocities have a significant impact on the final numbers calculated. The direct measurement of fluxes is difficult but this parameter is urgently required by the modellers.

4. Aquatic and Terrestrial Effects

Frankly, by yesterday morning we were totally disillusioned. We had heard that on the average our models are long-term but our data is short-term; our inventories are inadequate because they omit N, hydrocarbons, the $SO_2^{=}/SO_4$ ratio, etc.; our collectors are all mechanically defective. Well, that's research.

Then, Harold Harvey, in his opening remarks, stated that there is no case for acid rain killing fish. Essentially, he was saying that there is a need for more integrated research in fish studies, water chemistry, atmospheric deposition and terrestrial studies.

We need more cooperation in the calibrated watershed studies. Now, we run into problems that for the Algoma watershed site, two services and two departments are involved.

Another concern was raised by Sam Linzon. He stated that the impact of acidic precipitation may be greater on lakes where the surrounding soils are only marginally affected. Therefore, should our aquatic study sites be different from our terrestrial study sites?

Our second study site, Kejimkujik National Park, already has an APN station and ion balance studies. In addition, we plan to increase fish studies as well as other components. For our third site in Quebec, we have examined two locations. We plan to start work on this site in the next six months. The APN station will go in first and we hope to

obtain the cooperation of Quebec regional forestry people, IWD and Laval University. Our final site is the ELA. Everyone is fairly familiar with that study.

Another aspect in the aquatic area of our studies, is the survey of aquatic areas of Eastern Canada. M. Thompson is producing a very useful sensitivity map of eastern Canada based on judicious assessment of surface water chemistry derived from data in various archives.

All these studies are leading to negotiations with the Americans. Political and media pressures are still mounting and will probably peak during the ten days surrounding November 2, 1979. Before we can negotiate treaties with the U.S., we will need understanding between the provinces and the federal government. Still, field data takes one to two years to be worked up in a useful fashion. Policy workers need the data faster. So, we will have to develop a mechanism for passing information to the non-scientific users rapidly and with continuous updates. That will take discipline and will cramp the free style of the usual research environment.

It is perhaps an irony. On the one hand, we have a huge environmental problem here that is certainly complex and often baffling, and we are working under considerable research constraints. On the other hand, we are being pressed to action by responsibility centres which generally have neither grasped the extent of the problem (which is forgivable) nor grasped the cost in terms of environmental damage or possible control measures (which is not forgivable). These costs are orders of magnitudes

greater than the costs of all our programs put together. I think some of us will be giving a seminar or two in the executive sandbox.

After the completion of Dr. Martin's paper, the following discussion ensued:

NELS CONROY: Do your aquatic sensitivity maps include the new M.O.E. and M.N.R. data base?

FLOYD ELDER: Due to our deadline of July 1, for Ontario, we essentially used Ken Min's analysis of Ontario's data base.

NELS CONROY: That task is done then but it needs to be polished.

GORD McBEAN: Yes, but the sensitivity maps will be updated.

FLOYD ELDER: There will be an update around the end of this Fiscal Year.

NELS CONROY: Ontario's data will be computerized and available by the end of this fiscal year. The data base will contain from 3,000 to 4,000 lakes.

FLOYD ELDER: The purpose of the maps is to include them in the U.S./Canada LRTAP BRCG Report. The aquatic sensitivity maps show the extent of the problem areas in Canada but they contain no precise details of the location and number of lakes. We have encountered a phase problem with our U.S. counterparts. If we contract out for a more detailed analysis, there will be no U.S. counterpart. Also, the timescale for negotiations is currently unknown.

NELS CONROY: We may have to develop a formal mechanism so data can be freely transferred. Much of Ontario's and the federal data is raw data and thus, unavailable for internal use due to priorities. We need to develop a mechanism as soon as possible to cover this problem. Someone has to make a policy decision to hold data.

FLOYD ELDER: We have not encountered this problem yet. Our data bases are not easily accessible; much is still in notebook form. There is a problem, however, with the compatibility of data and data bases.

JIM KRAMER: What is the basis for the design of such susceptibility maps? I do not have a clear opinion of what constitutes a susceptible lake. John Allin's definition of an alkalinity of 300 µeq. is too high. Your interpretation of these maps will depend on your basis for susceptibility. Is it possible to circulate your basis for susceptibility on which your maps have been designed for comments from various consultation groups?

FLOYD ELDER: Yes, we agree to receiving such comments. But, what other criteria can be used? If we base it on alkalinity, we come up with lakes that are very sensitive, moderately sensitive and insensitive. Then, we have to define the rate of loss. What is the timeframe? We need models to relate alkalinity to rates of degradation. It is difficult to send a document out for scientific scrutiny before it is used.

GORD McBEAN: This type of material is not restricted to discussion. It expresses the views of that group of scientists at that time. There is nothing in it that is not already in the literature.

GREGG VAN VOLKENBURGH: Because of all the negotiations and policy discussions regarding this issue, we need to include a new area in our programs, the coordination of information. This could take the form of a newsletter perhaps which lists all related publications by the universities, the province of Ontario, the federal government and other provinces. It is also an excellent mode to inform scientists of any related conferences.

DOUG WHELPDALE: I will discuss the possibility with Bob Slater of compiling a bibliography on acid rain. We should request comments from the EPS librarian under contract to establish the scope of the issue.

GREGG VAN VOLKENBURGH: What is the possibility of establishing a physical library on acid rain?

HANS MARTIN: With respect to doing a bibliography in report form, it should be the responsibility of the coordinating group of this conference.

LOU SHENFELD: Changing the topic, do your transformation processes include a study of in-cloud formation of acid rain?

HANS MARTIN: Yes.

DOUG WHELPDALE: To a limited extent. It is difficult to decide the altitude at which one should start working. In Europe, aircraft flights

have been used to verify long range transport models. They prove to be very inefficient and costly. We have a budget of under $25,000 to do an in-cloud study of gas and particles on a regional scale along the borders near Lake Ontario and Lake Erie. However, in-cloud studies are not of a high priority at this time.

FLOYD ELDER: Justification has to exist for air pollution research other than LRTAP and acid rain.

LOU SHENFELD: We need hard data for justification rather than just models. It is vital that we do research on where and at what altitude to carry out these studies.

c) M.N.R. Fiscal 1980/81 LRTAP Program - J. Allin

For a detailed version of J. Allin's presentation, refer to Appendix Twenty-Four.

At the completion of Dr. Allin's presentation, the following discussion occurred:

WES LAMMERS: Did you attempt to find a species resistant or more tolerant to acidity?

JOHN ALLIN: That is not a major objective of our program but it is an area worth pursuing. We did discuss a selective breeding program.

TOM BRYDGES: What is the role of the Hamilton Lake experiment in the liming program?

JOHN ALLIN: It is a necessary experimentation in order to establish the feasibility of liming. Success in this area has been carefully documented but our concern is that we will be pushed into remedial measures that have not been properly investigated.

JACK DONNAN: Are the M.N.R. forestry people investigating the effects of acid precipitation on vegetation?

JOHN ALLIN: I am not aware that they are presently investigating this area. Work was done in Sudbury several years ago relating to fumigations.

IAN MORRISON: No one is currently involved in this field as it is not perceived in forestry circles as a major problem. The forestry resources in general are already stretched to their limit.

JACK DONNAN: What about acidic precipitation as related to regeneration?

IAN MORRISON: That is not thought of as a problem.

SAM LINZON: With respect to seed germination in the forests in the Sudbury area, regeneration is good where the trees were killed. Acidification helps break the seed coats and is considered as a positive effect.

JOHN ALLIN: I've mentioned that on a number of occasions.

LEN MAKI: What fraction of the lakes in the areas you have chosen to survey will you actually cover?

JOHN ALLIN: I do not know at the moment. This fall we will assemble the data we have collected so far for further interrogation before making our final decision.

LEN MAKI: Do you choose your sampling areas on the basis of the mean pH of precipitation?

JOHN ALLIN: This year's areas were chosen in that manner because those areas were thought to be more sensitive. However, we plan to look at non-sensitive areas as well.

ED PICHE: The choice of areas for sampling is related to the currently known acidity of precipitation in that area.

GREGG VAN VOLKENBURGH: Are your programs complementary to Norway's research?

JOHN ALLIN: That is a major objective of the A.P.I.O.S. program.

ED PICHE: However, currently it is only in its embryonic stage.

GREGG VAN VOLKENBURGH: Such complementary research would give legitimate reasons for pursuing research in certain areas and not in others.

JOHN ALLIN: We are in the initial stages, trying to determine the most feasible alternatives.

ED PICHE: We recognize that there is inertia in the system but we are gearing our resources as best as possible.

JACK DONNAN: Is the Wildlife Branch planning any related studies?

JOHN ALLIN: They have expressed an interest and have had some input into the M.O.E.'s submission to Cabinet. Presumably, some research will go on in this area.

c) Federal DFO LRTAP Program - R. Thomas

The Department of Fisheries and Oceans is suffering from dual tunnel vision and thereby focussing most of its attention on the waters to the east and west of Canada. As a result, we are encountering some difficulty and frustration in developing a fisheries component to the LRTAP Program. The major problem is the question of funding. To date, we have received zero base reallocation. The fisheries component never received any funding whereas the environmental program received appropriate funding. Therefore, we are lacking an integrated approach.

Due to these problems, the Department decided to take action and make some Treasury Board Submissions. The LRTAP national program is holding an assessment of the program and we would like to have an input. The Central Region of the DAS is taking a look at the biolimnology laboratory in order to develop a program for regional responsibility. We plan to stress a greater research emphasis on contaminants

subject to bioaccumulation and biomagnification. Fish exist but are inedible and we need to deal with this problem. One route could be an extension of the Great Lakes Study.

It is gratifying to see and hear the enthusiasm evident at this meeting and in the development of the various programs. However, it is easy for such enthusiasm to get out of control and we may end up with a massive expenditure that gives us little return. Therefore, I think we need to develop a sound system for program evaluation to ensure that we receive value for our dollars invested.

Dr. Thomas' presentation generated the following discussion:

HANS MARTIN: It is the federal responsibility to assess the LRTAP program which is not necessarily limited to acidic precipitation. Other contaminants are involved as well.

MARIS LUSIS: Can you name some specific contaminants as examples?

RICK THOMAS: Some examples are lead and PCB's. Sixty percent of lead comes from the atmosphere and fifty percent of PCB's comes from the atmosphere. As a result, there is a high contamination of fish in areas remote from industrial development.

FLOYD ELDER: The highest contamination of PCB's is at Bachewana which is remote from any likely sources.

GREGG VAN VOLKENBURGH: The provincial PCB survey for two to three weeks resulted from the St. Lawrence cement problem and led to a province wide survey where 24 hour values were recorded every day at 25 sites. The values were then compared to synoptic weather systems. We plan to do the survey again in the wintertime. However, it will be necessary to collect a lot of water in order to do all the analyses necessary for organic compounds.

RICK THOMAS: In the original scientific program, many parameters were included. The way the LRTAP program is currently running is not the way it was originally envisaged. Emphasis is being placed on protecting the 200 mile limit.

LOU SHENFELD: At the recent OECD meeting, the British stressed that the end result of LRTAP on vegetation is an added growth derived from the S and N emissions to the atmosphere.

JIM KRAMER: I wish you luck on your PCB synoptic weather system work; it will be difficult since PCB's are already ubiquitous. It may be a case where deposition and reemission are occurring. As a result, it may only be an analytical contamination problem.

RICK THOMAS: PCB's are volatilizing from various areas and their actual transport routes may be different from those predicted.

3. Open Discussion - Discussion of Future Meetings

a) Terms of Reference for Ontario - Canada LRTAP Research Coordination Group - F. Elder

To begin with, Mr. Elder read two excerpts from letters received commenting on the use of such meetings. These two letters essentially covered a range of opinions, from very good to a "waste of time".

The first question to be raised is does the RCG, as part of its functions, require such meetings? If so, how should the attendance be handled?

1. As in this case, by invitation only. For this meeting, we invited government agency scientists, government agency managers, and University contract scientists. As a result, we excluded industrial research scientists, consultant firms, University staff not under contract and research students.

2. Open attendance as in a public meeting. Various difficulties arise when considering this type of forum.

Another point of discussion raised by Mr. Elder was the establishment of terms of reference for the BRCG. The proposed terms of reference are:

1. to encourage intercommunication among the various scientists involved.

2. to encourage cooperative programs.

3. to identify program weaknesses and gaps.

4. to encourage communicative feedback from scientists to management.

At this point, the above questions were put to the floor for discussion:

DAVE BALSILLIE: What is the BRCG and who is on it?

GORD McBEAN: Mr. Drowley and Dr. Collin held a meeting and agreed to form the BRCG to establish communication between the federal and Ontario LRTAP researchers.

In the initial letter, the membership was composed of:

Ontario	Federal
Ed Piche	Floyd Elder
Tom Brydges	Hans Martin
Maris Lusis	Gord McBean

The group's first meeting was held as part of a larger group.

NELS CONROY: I think it was remiss on the part of the organizers not to involve the fisheries people especially since the major impactor is fish.

ED PICHE: These limitations were recognized immediately and there will be some expansion of the initial membership.

GORD McBEAN: Since the fisheries people are outside the departments represented by the M.O.E. and D.O.E., we hesitated to commit anyone in this area by name.

FLOYD ELDER: We can recommend that the membership be reviewed.

JACK DONNAN: I am in a state of confusion after this three day meeting. We seem to be focussing

on acidic precipitation but the problem is referred to as LRTAP. If, essentially, the overall problem is the long range Transport of Air Pollutants, then not only should the fisheries people be represented on the RCG, but the membership should be expanded to Health, Abatement and other areas. Therefore, I think we need a clear definition of the problem.

GREGG VAN VOLKENBURGH: I recommend that Ontario change the name of its program.

ED PICHE: If we define the study as having a much broader scope, then the name will have to be changed to cover the true scope.

FLOYD ELDER: Acid rain is the core issue but other areas are associated with it.

GREGG VAN VOLKENBURGH: Then it's another case of tunnel vision. The terms of reference need to be clearly defined.

FLOYD ELDER: We are not including urban or industrial air pollution.

JACK DONNAN: What about ozone?

LOU SHENFELD: Ozone is included in the long range transport of oxidants.

ED PICHE: Initially, the study was called A.P.I.O.S. because it dealt with the acidic precipitation problem. If Ontario broadens its scope, the name

will be changed. In the case of the federal government, acidic precipitation is dealt with under the umbrella study of LRTAP.

JIM KRAMER: Still, the H^+ ion is the master variable. We are creating arbitrary boundaries on the technical aspects. I do not see the titles of the programs as problematic.

FLOYD ELDER: If we exclude urban industrial air pollution, we exclude most of the health effects.

IAN MORRISON: I would like to change the direction of the conversation. I feel we should expand the program to include the portion of Northern Ontario that is West of Highway 7. We should contact Cal Sullivan.

LEN BARRIE: The problem is acidic deposition and not limited to acidic precipitation. We should be focussing on all types of deposition.

GREGG VAN VOLKENBURGH: The dry deposition aspect is virtually ignored.

GORD McBEAN: This meeting was held to deal solely with acidic precipitation. However, the federal program has a broader mandate with acidic precipitation as first priority, toxic metals as second and persistent inorganic contaminants as third.

LOU SHENFELD: Was the RCG formed on the basis of acidic precipitation or LRTAP?

GORD McBEAN: It was agreed to on the basis that it would establish better discussion and communications in areas of mutual interest.

b) Usefulness of Such a Forum

At this time, Mr. Elder requested comments on the usefulness of such a forum.

JACK DONNAN: I think we need to be more specific in the terms of reference.

SAM LINZON: The terms of reference discussed are for the BRCG and are not for this group here.

LOU SHENFELD: Acidic Precipitation was understood to be the subject matter of this meeting. The objectives of the federal/provincial group is to define and solve the problem jointly.

HANS MARTIN: The purpose of the BRCG is to facilitate the functions of the two programs.

LOU SHENFELD: Each group is working towards the objectives of its individual program.

HANS MARTIN: Yes, but on a common ground.

LOU SHENFELD: The BRCG has been established to avoid duplication as well.

ED PICHE: Let us leave this issue by stating that an agreement was reached that the terms of reference for the BRCG need to be defined more explicitly.

DOUG WHELPDALE: If we take the assumption that the Ontario/Canada RCG has as its primary purpose to enhance communications between the two programs, then this meeting should at least result in recommendations to the RCG of areas to consider

for future work. We can arrange for some joint projects to be undertaken and then report back at the next meeting. For example, we can organize some cooperation on the basis for drawing sensitivity maps. We can draw on the appropriate sources of information that are available.

HANS MARTIN: We have already identified the need for cooperative efforts in the computer modelling area. Other areas for possible coordination raised at this meeting are the PEPE experiment and library activity.

LOU SHENFELD: We need a mechanism to facilitate the exchange of data, a list perhaps of whom to contact to obtain data in a specific area.

JIM KRAMER: We also mentioned a common usable data base for valuable network deposition information. I would like to add to Doug's comment that if the RCG does not facilitate communication between the two programs, then no other agency will.

LEN BARRIE: The first term of reference for the RCG can be carried out without it.

JIM KRAMER: If we feel contact or communication is necessary, then we simply hold another seminar.

At this point, Floyd Elder interjected to turn the conversation back to the usefulness of such seminar meetings. The function of communication between various program researchers is not served by a large meeting of, for example, the American Chemical

Society, nor by a workshop such as the one held at Sundridge. This seminar has encouraged communication between scientists of various disciples as well as between the federal and provincial representatives. Mr. Elder again requested comments regarding the usefulness of such a seminar.

GREGG VAN VOLKENBURGH: I found the past three days to be very useful and feel that the time was well spent. I think that we should continue to hold such seminars. There is no need to travel to Washington in order to hear what other agencies in Canada are doing. It is necessary to develop a national cohesion across the various disciplines. We deserve to have the opportunity to communicate with other groups involved in similar research and three days per year for such a seminar and an exchange of information are well worth the money invested.

LOU SHENFELD: I agree with Gregg but feel that outsiders with strong expertise in certain areas should also be invited to offer a critique of the programs.

ED PICHE: Perhaps we should put money aside to invite known experts.

GREGG VAN VOLKENBURGH: We could invite representatives from Ontario Hydro and the Ministry of Health.

LOU SHENFELD: In addition, I think we should consider inviting a top air pollution modeller, biologist and geochemist from outside our programs to hear their views.

JACK DONNAN: More effort is needed to involve Quebec and the Maritime provinces.

GORD McBEAN: There is an Atlantic regional meeting scheduled for next month.

JIM KRAMER: I found this seminar to be a valuable learning experience. A lot of information was exchanged and we are left with many ideas for consideration. Therefore, the time was well spent. I hope we continue to hold this type of seminar.

TOM BRYDGES: This seminar had a planning function as well as other functions. Before we expand our areas of research, we need to pull our collective acts together. By Christmas, all the budgets will be finalized, gaps in the program will be realized and as a result, we may need to restructure our programs. Then, we may need to hold another planning meeting. As well, we may then be in a position for a meeting where more technical papers can be presented and perhaps the technical meeting membership can be expanded to include more representatives from Quebec and the Maritimes.

DAVE BALSILLIE: I agree with Tom. This seminar had as one of its functions to exchange program information. It is frustrating to people within the program not to know what the other disciplines are doing. There was more data description than program description at this meeting.

TOM BRYDGES: I can foresee the need for two types of meetings.

GREGG VAN VOLKENBURGH: Vehicles already exist for technical information exchanges. As well, a number of committees have been established to deal with this issue.

DOUG WHELPSDALE: I agree. There are other mechanisms for the presentation of scientific results. If we focus on such an exchange, these meetings will become another symposium series. We already have many ways to report our progress in particular areas. I think we should start to focus on more specific problems that need to be solved.

HANS MARTIN: For example, there was an LRTAP meeting held by the Atmospheric Meteorological Society where scientific results were exchanged.

LOU SHENFELD: But the opportunity for informal discussion is limited at such large technical meetings. At a seminar such as this one, we do not have to worry about the press when communicating information or identifying shortcomings. Scientific results were presented at this seminar and at the next meeting, more results could be given.

LEN BARRIE: I agree with Doug. We had a good mixture of people here; some are actively involved in the scientific work and others are at the intermediate management level. When tapping "foreign" expertise for critiques, we should use that route.

LOU SHENFELD: Two outsiders will not cover all phases of the problem.

LEN BARRIE: We could invite a representative from the Norwegian research group to give us guidance.

LOU SHENFELD: Which will keep us from repeating their mistakes.

FLOYD ELDER: Worldwide experts have been invited to the Atlantic meeting. That group has been keeping close contact with world experts but there does not appear to be much new information from that source. Still, the Atlantic region is more isolated and researchers lack the opportunity to attend the same meetings we do.

SERGE VILLARD: I'm not sure of the need for outside experts to attend our seminars. There is perhaps a need to have an expert on liming, for example Tom Brydges, explain the issues involved to this group.

TOM BRYDGES: The federal/provincial RCG may wish to follow that up.

NELS CONROY: Since the agenda for this seminar was both informal and structured, we have managed to succeed at this meeting. I think our success would be diluted by having a large meeting such as the Atmospheric Chemistry Society's meetings.

LOU SHENFELD: I think we should still invite two or three more people.

SERGE VILLARD: I agree.

BOB VET: Each group here has a responsibility to an overall program. We need to combine background

research and peer review but I do not see the use of bringing in one person to evaluate an overall program.

LOU SHENFELD: We have two outsiders here already. What difference will two or three more make?

WALTER CHAN: Outsiders can identify any gaps or weaknesses in our programs and give technical presentations in their field. Peer review should be on a separate basis.

TOM BRYDGES: I recommend that the RCG resolve the issue of identifying gaps and weaknesses in the two programs.

GORD McBEAN: I do not think it would be useful to bring in experts from other jurisdictions. We are having a frank discussion now but outside experts might stifle such a free discussion.

GREGG VAN VOLKENBURGH: At a recent MAP3S progress meeting, a peer group reviewed the program. Len is on this committee and perhaps he could comment on the usefulness of such peer review.

LEN BARRIE: In this case, there was a progress review for the purposes of management. The scientists presented their work in detail and were open to both verbal and written criticism.

FLOYD ELDER: I think that an external peer review of our two programs would be useful but not in the context of this kind of meeting.

HANS MARTIN: I think we should be looking at student participation. If we allow students to participate here, we will essentially be developing our resources.

c) Limitations on Meeting

At this point in the discussion, Mr. Elder proceeded to summarize what he felt was the consensus of opinion expressed by the participants at this seminar regarding future attendance of such seminars:

1. to extend the boundaries of this group within reasonable limits.

2. to exclude government NRC supporters.

LOU SHENFELD: Could you explain the rationale behind including university consultants but excluding company consultants?

FLOYD ELDER: Consulting firms have a tendency to attempt to advertise their wares at such seminars and to look for future funds.

NELS CONROY: I would like to change the topic for a minute and address a question to the organizers of this seminar. Did you feel that you achieved the objective of this meeting? Where were the objectives defined?

FLOYD ELDER: I feel that we achieved the purpose for the meeting and more besides.

ED PICHE: We achieved a cross-fertilization of ideas and information and as well, I think we managed to inform the regional people as to the status of A.P.I.O.S. They can now hold internal meetings and pass the information on to others in their region. I personally now have a better understanding of many formerly vague but complex ideas, i.e. the aluminum issue, and am better prepared to argue on a technical basis for or against certain proposals.

JIM KRAMER: Regarding the question of whether or not to invite external consultants, I think the conference organizers should invite a consultant if he can add to any topic under discussion at the meetings. Operationally, the organizers should ask various people to chair sessions and present papers. As to the general attendance, I think you should advertise for a limited number of participants and accept applicants on the basis of contributions. As well, I agree that research students can contribute in certain areas and should be allowed to attend, again on the basis of contribution.

LOU SHENFELD: That type of arrangement sounds like the Gordon Conference held in the States where attendance is limited to 50 participants based on contribution.

ED PICHE: I think the leeway for attendance is great and should be determined once the focus of the meeting is decided.

WES LAMMERS: I agree and feel that more emphasis should be placed on the socio-economic aspects at the next meeting.

d) Location and Time of Next Meeting

FLOYD ELDER: This meeting served a broad purpose whereas the next meeting will probably have a smaller focal point. I think meetings should be called according to the need for them.

GREGG VAN VOLKENBURGH: I have a suggestion for the next general meeting and, that is, that it should be set up similar to a Gordon type Conference for information exchange within the Canadian scientific community on LRTAP. I think it should be held about one year from now.

FLOYD ELDER: Regarding the actual time of year, I think it would be more convenient to hold the meeting in the wintertime.

JIM KRAMER: That is the off season for resorts but remember that we university people go back one or two weeks after Labour Day for the winter term.

GREGG VAN VOLKENBURGH: The summer is the season for most of our field studies and in the autumn we are busy preparing our fiscal budgets for the next year. How about reading week in February?

FRANK HICKS: The first week of December is the traditional conference week for the Ministry of Natural Resources. It's a good time of year for conferences.

It was concluded that the RCG would decide on the need for a meeting on a certain subject and on the usefulness of inviting external consultants. Input from the participants at this meeting is encouraged. The next meeting will be announced when the RCG has decided on the subject and date.

JIM KRAMER: What about the length of these meetings?

FLOYD ELDER: We were limited in this case by the travel time involved.

JIM KRAMER: I felt that we had a better discussion going in the last two evening sessions. The first two daily sessions were more of a a general information exchange while the two evening sessions were more of a technical exchange. We should have the rest of Thursday to write out a report.

FRANK HICKS: In the liming session, we had a disproportionate amount of discussion time which is the boon of such a meeting. I would like to recommend that at future meetings, you do not cut down on informal discussion time.

FLOYD ELDER: It was the intent of the session chairmen to keep the discussions going in the right direction but as informal as possible.

ED PICHE: Mr. Elder and myself would appreciate any written comments or criticisms on any aspects of this meeting.

4. Session Recommendations

1. Terms of reference for the BRCG need to be defined more explicitly by senior officials as soon as possible.

2. Ontario should change the name of its program to broaden its scope similar to the Federal LRTAP program.

3. The program coordinators should prepare an overall LRTAP bibliography and update it annually.

4. This kind of meeting is very useful and should be encouraged and supported by senior management of all governments. Meetings of this nature should be held as often as deemed necessary by the program scientists and should be organized and arranged by the program coordinators.

5. Participation should be limited and by invitation only. However, relevant presentation should be solicited from outside agencies when deemed approriate and beneficial. e.g.:

   (i) Reports by graduate students involved in related research.

   (ii) Presentations by acknowledged outside experts.

   (iii) Presentations by Hydro officials or officials from other ministries or agencies.

6. Participation by representatives from other provinces should be encouraged.

III LIST OF APPENDICES

1. Policy Development Schematic

2. L.R.T.A.P. Areas of Concern

3. Ontario Pollutant Inventory Information

4. Canadian Inventories of Sources and Emissions of Sulphur Dioxide and Nitrogen Oxides

5. Mathematical Modelling

6. Comparison Between Measured and Computed Concentration of Sulphur Compounds in Eastern North America

7. The Prediction of Rain Acidity and SO_2 Scavenging in Eastern North America

8. Provincial Acid Precipitation Deposition Network

9. Deposition of Nutrients and Major Ions by Precipitation in South-Central Ontario

10. Heavy Metal Deposition

11. National Atmospheric Chemistry Network

12. Great Lakes Basin - The CANSAP Network

13. Great Lakes Basin - The CCIW Network

14. Alkalinity Methodology as Related to Soft-Water Measurements

15. Preliminary Results of Lake Susceptibility Surveys

16. Aquatic Setting of the Algoma Area Watershed Studies

17. Chemistry of Turkey Lake Basin

18. Terrestrial Environment of the Algoma Watershed Study

19. Acid Rain Investigations on Three Lake Basins in Kejimkujik National Park, N.S.

20. Aluminum in Low pH Waters - Some Preliminary Results

21. Alkalinity Deficiency as an Index of Acidification

22. The Economic Implications of Acid Precipitation

23. An in situ Experiment Using Limestone to Enhance the Hatching Success of Rainbow Trout (Salmo gairdneri) Eggs in an Acid Lake

24. M.N.R. 1980/1981 L.R.T.A.P. Program

IV LIST OF PARTICIPANTS

Code: A - Academic Representative
F - Federal Representative
P - Provincial Representative

NAME	ADDRESS	TELEPHONE
Dave Aitkens (P)	Ministry of the Environment Southeastern Region 133 Dalton St. Kingston, Ontario K7L 4X6	(613) 549-4000
J. T. Allin (P)	Ministry of Natural Resources Fisheries Branch Whitney Blk., Queen's Park Toronto, Ontario M7A 1W3	(416) 965-7883
David Balsillie (P)	Ministry of the Environment Northeastern Region 469 Bouchard St. Regency Mall Sudbury, Ontario P3E 2K8	(705) 522-8282
Len Barrie (F)	Atmospheric Environment Service 4905 Dufferin St. Downsview, Ontario M3H 5T4	(416) 667-4796
T. Brydges (P)	Ministry of the Environment Water Resources Branch Hwy. 401 & Islington Toronto, Ontario	(416) 248-3058
John Casselman (P)	Ministry of Natural Resources Fisheries Research Section Box 50 Maple, Ontario L0J 2M0	(416) 832-2761
C. H. Chan (F)	Inland Waters Directorate Department of Environment 867 Lakeshore Rd. P.O. Box 5050 Burlington, Ontario L7R 4A6	(416) 637-4641

Walter Chan (P)	Ministry of the Environment Air Resources Branch 880 Bay St. Toronto, Ontario M5S 1Z8	(416) 965-1634
Nels Conroy (P)	Ministry of the Environment Northeastern Region 266 Caswell Dr. Sudbury, Ontario	(705) 522-8282
J. M. Cooley (F)	Great Lakes Biolimnology Laboratory Canada Centre for Inland Waters 867 Lakeshore Rd. P.O. Box 5050 Burlington, Ontario L7R 4A6	(416) 637-4202
Peter Dillon (P)	Ministry of the Environment Water Resources Branch Limnology & Toxicity Section Box 213 Rexdale, Ontario	(416) 248-3058
Jack Donnan (P)	Ministry of the Environment Program Planning Branch 135 St. Clair Ave. West Toronto, Ontario M4V 1P5	(416) 965-7984
Floyd Elder (F)	Department of the Environment National Water Research Institute Canada Centre for Inland Waters 867 Lakeshore Road Box 5050 Burlington, Ontario L7R 4A6	(416) 637-4303
Glen Grosse (P)	Ministry of the Environment Southwestern Region 985 Adelaide St. South London, Ontario N6E 1V3	(519) 681-3600
John Gunn (P)	Ministry of Natural Resources P.O. Box 3500 Station "A" Sudbury, Ontario	(705) 522-7823

H. H. Harvey (A)	University of Toronto Department of Zoology Ramsay Wright Zoological Labs 25 Harbord St. Toronto, Ontario M5S 1A1	(416) 978-3504
Frank Hicks (P)	Ministry of Natural Resources P.O. Box 219 Whitney, Ontario K0J 2M0	(705) 637-2780
James Hornick (P)	Ministry of the Environment Information Services Branch 135 St. Clair Ave. W. 6th Floor Toronto, Ontario M4V 1P5	(416) 965-7117
Dean S. Jeffries (P)	Ministry of the Environment Water Resources Branch Resources Road Rexdale, Ontario	(416) 248-3058
M. G. Johnson (F)	Great Lakes Biolimnology Laboratory Canada Centre for Inland Waters 867 Lakeshore Road P.O. Box 5050 Burlington, Ontario L7R 4A6	(416) 637-4548
Laura Johnston (F)	Inland Waters Directorate Department of the Environment Ottawa, Ontario	(613) 995-4031
W. Keller (P)	Ministry of the Environment Northeastern Region 266 Caswell Dr. Sudbury, Ontario	(705) 522-8282
J. R. M. Kelso (F)	Great Lakes Biolimnology Laboratory 875 Queen East Sault Ste. Marie, Ontario	(705) 942-2848
Joe Kerekes (F)	Canadian Wildlife Service c/o Biology Department Dalhousie University Halifax, Nova Scotia	(902) 426-3430

James R. Kramer (A)	Department of Geology McMaster University Hamilton, Ontario	(416) 525-9140 (Ext. 4514)
Tony Kwain (P)	Ministry of Natural Resources Fisheries Research 875 Queen St. East Sault Ste-Marie, Ontario P6A 2B3	(705) 942-1411
Wes Lammers (P)	Ministry of the Environment Central Region 150 Ferrand Drive Don Mills, Ontario M3C 3C3	(416) 424-3000
Sam Linzon (P)	Ministry of the Environment Air Resources Branch 880 Bay Street Toronto, Ontario M5S 1Z8	(416) 965-4516
Barry Loescher (P)	Ministry of the Environment Laboratory Services Branch Resources Road Toronto, Ontario	(416) 248-3346
Maris Lusis (P)	Ministry of the Environment Air Resources Branch 880 Bay Street Toronto, Ontario M5S 1Z8	(416) 965-1634
Jim MacLean (P)	Ministry of Natural Resources Fisheries Research Section Box 50 Maple, Ontario L0J 2M0	(416) 832-2761
L. W. Maki (P)	Ministry of the Environment Northwestern Region 435 James St. S. Thunder Bay, Ontario P7C 5G6	(807) 475-1215
Gordon McBean (F)	Atmospheric Environment Service 4905 Dufferin St. City of North York Downsview, Ontario M3H 5T4	(416) 667-4789

Hans Martin (F)	Atmospheric Environment Service 4905 Dufferin Street City of North York Downsview, Ontario M3H 5T4	(416) 667-4824
P.K. Misra (P)	Ministry of the Environment Air Resources Branch 880 Bay St. Toronto, Ontario M5S 1Z8	(416) 965-1634
J. C. Mittermayer (P)	Ministry of the Environment 40 St. Clair Ave. W. 6th Floor Toronto, Ontario M4V 1P5	(416) 965-1140
Ian K. Morrison (F)	Canadian Forestry Service 875 Queen East Sault Ste. Marie, Ontario	(705) 949-9461
E. W. Piche (P)	Ministry of the Environment 40 St. Clair Ave. W. 6th Floor Toronto, Ontario M4V 1P5	(416) 965-1140
Mike Powell (P)	Ministry of Natural Resources Northeastern Region 174 Douglas St. Sudbury, Ontario P3E 1G1	(705) 673-1111
Hank Rietveld (P)	Ministry of Natural Resources Algonquin Region Box 9000 Huntsville, Ontario P0A 1K0	(705) 789-9611
John Robinson (A)	Environmental Biology University of Guelph Guelph, Ontario	(519) 824-4120 (Ext. 3828)
Wolfgang A. Scheider (P)	Ministry of the Environment Water Resources Branch Resources Road Toronto, Ontario	(416) 248-3058
Lou Shenfeld (P)	Ministry of the Environment Air Resources Branch 880 Bay St. 4th Floor Toronto, Ontario M5S 1Z8	(416) 965-0689

R. L. Thomas (F)	Great Lakes Biolimnology Laboratory Canada Centre for Inland Waters 867 Lakeshore Road P.O. Box 5050 Burlington, Ontario L7R 4A6	(416) 637-4568
Mary Thompson (F)	Canada Centre for Inland Waters National Water Research Laboratory 867 Lakeshore Road P.O. Box 5050 Burlington, Ontario L7R 4A6	(416) 637-4213
Frank Tomassinni (P)	Ministry of the Environment Hwy. 401 & Islington Toronto, Ontario	(416) 248-3512
Ken Trent (P)	Ministry of the Environment West-Central Region 140 Centennial Pkwy. N. Stoney Creek, Ontario L8E 3H2	(416) 561-7410
Gregg Van Volkenburgh (P)	Ministry of the Environment Air Resources Branch 880 Bay St. Toronto, Ontario M5S 1Z8	(416) 965-2053
Frank Vena (F)	Environmental Protection Service Air Pollution Control Directorate Place Vincent Massey Ottawa-Hull, Ontario K1A 1C8	(819) 997-3352
A. Venkatram (P)	Ministry of the Environment Air Resources Branch 880 Bay St. 4th Floor Toronto, Ontario M5S 1Z8	(416) 965-5068
Bob Vet (P)	Ministry of the Environment Air Resources Branch 880 Bay St. Toronto, Ontario M5S 1Z8	(416) 965-1634

Yvan Vigneault E.C. (F)	Inland Waters Direcotrate Quebec Region 2700 Blvd. Laurier P.B. 10,000 Ste-Foy, Quebec	(418) 694-3921
S. Villard (P)	Ministry of the Environment Laboratory Services Branch Resources Road Toronto, Ontario	(416) 248-3036
Eva Voldner (F)	Atmospheric Environment Service 4905 Dufferin St. City of North York Downsview, Ontario M3H 5T4	(416) 667-4780
Cal Warden (P)	Ministry of Natural Resources Mines Group Whitney Block 4th Floor Queen's Park Toronto, Ontario M7A 1W3	(416) 965-1311
D. M. Whelpdale (F)	Atmospheric Environment 4905 Dufferin St. North York, Ontario M3H 5T4	(416) 667-4785

V. BUDGET SUMMARY

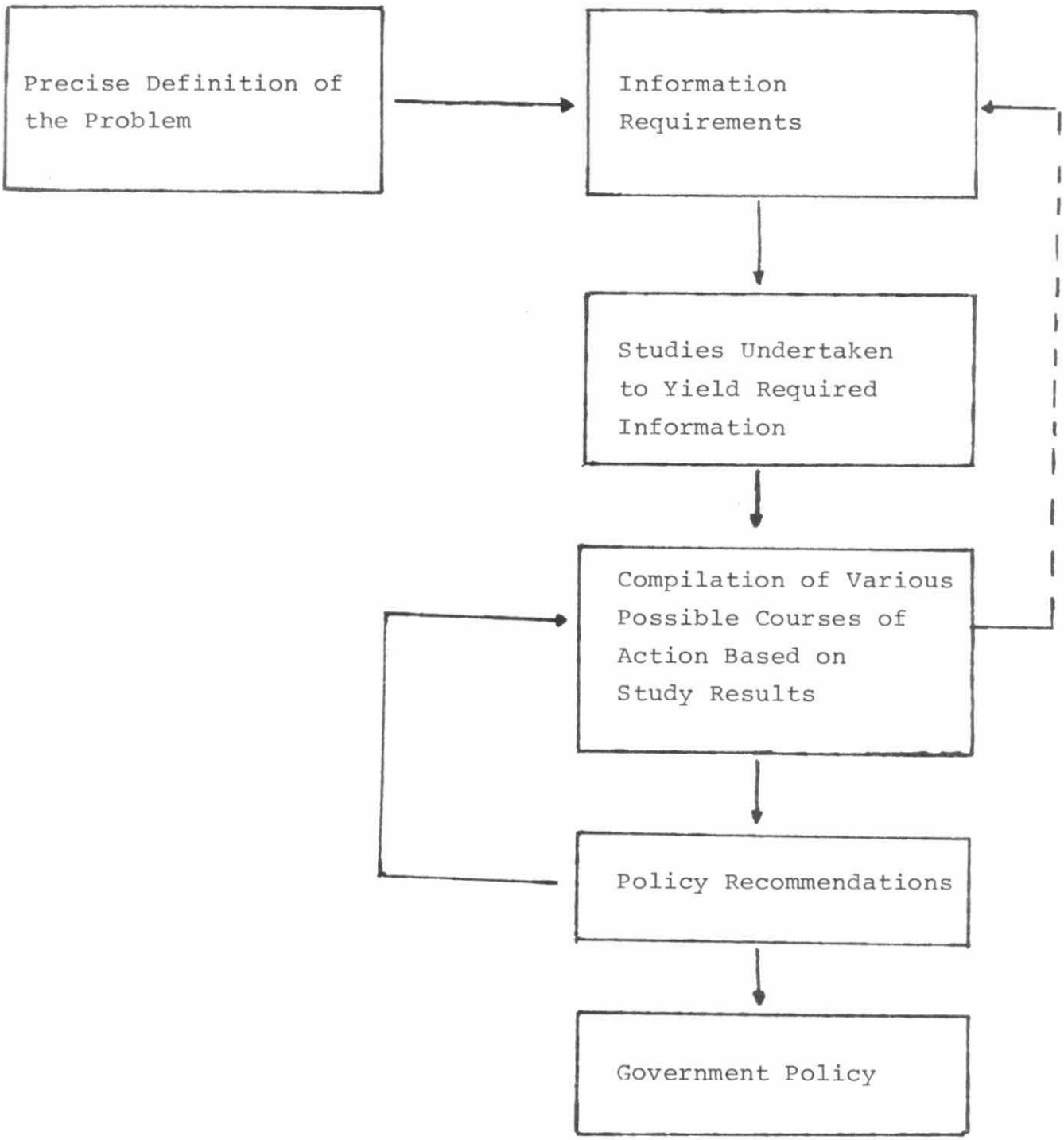
Breakdown of Costs:

Seminar Room	$ 75.00
Wine and Cheese Reception	375.00
Snacks for two evenings	300.00
Coffee	75.00
Total:	$825.00

These costs were divided between the Federal Atmospheric Environment Service and the Ontario Ministry of the Environment.

APPENDIX ONE

POLICY DEVELOPMENT SCHEMATIC


Precise Definition of the Problem
Information Requirements
Studies Undertaken to Yield Required Information
Compilation of Various Possible Courses of Action Based on Study Results
Policy Recommendations
Government Policy

APPENDIX TWO

L.R.T.A.P. AREAS OF CONCERN

I. Sources and Source Strengths (SO_2 + NO_x)

a) Inclusion of nitrogen compounds in L.R.T.A.P. modelling. (T. Munn)

b) Develop a continuous monitor of ambient ammonia gas and then monitor ambient concentrations at several sites in eastern Canada for one year. (A.E.S.)

c) Monitor the concentrations of particulate trace elements at a "regionally representative" site in Southern Ontario on a daily basis for one year. (A.E.S.)

d) Determination of a relationship between precipitation amount (6-24 h) and pollutant concentration in the precipitation at precipitation chemistry monitoring sites in North America (i.e. scavenging coefficient as a function of precipitation intensity). (A.E.S.)

e) Acquisition of a good data base for determining the optimum period for collecting precipitation samples, i.e. must they be collected on an event basis, or is monthly collection O.K.? (M. Lusis)

f) Development of an NO_x model. (Choquette)

II. Meteorology - Atmospheric Transport Including Physics and Chemistry
- oxidation rate
- aerosol formation kinetics
- absorption phenomena
- potential synergisms with copollutants
- modelling.

a) Inclusion of nitrogen compounds in L.R.T.A.P. modelling. (Munn)

b) Event studies of precipitation chemistry as a function of meteorological conditions. (A.E.S.)

c) Improvement in methods for parameterizing atmospheric transformation and deposition processes, especially for sulphur and nitrogen compounds. (Lusis)

d) Development of an NO_x model. (Choquette)

e) Investigate the fraction of total nitrate in the atmosphere that is composed of nitric acid gas. (A.E.S.)

f) Determination of monthly average variations in pollutant emissions about the annual mean emissions as a percentage, and the determination of any diurnal variation in emissions as a function of time of day covering North America. (A.E.S.)

III. Deposition (Sinks)

- dry gaseous
- dry particulate
- modelling
- wet rain
- wet snow

a) Inclusion of nitrogen compounds in L.R.T.A.P. modelling. (Munn)

b) Review of parameterization of transformation and deposition processes involving nitrogen oxides. Presented in such a form that immediate incorporation into L.R.T.A.P. models would be possible, and determine type of model required. (A.E.S.)

c) Measure the dry deposition inputs of SO_2, HNO_3, NH_3 gases and $SO_4^{=}$, NO_3^{-} in particulate matter to selected Canadian watersheds. (A.E.S.)

d) Study pH changes and stability of precipitation samples collected at Canadian sites, in order to apply errors to depositions calculated from the data being collected in Canadian networks. (A.E.S.)

e) Production of a grid point array of dry deposition velocities for various pollutants covering North America (perhaps on a seasonal basis). (A.E.S.)

f) Improvement in methods for parameterizing atmospheric transformation and deposition processes, especially for sulphur and nitrogen compounds. (A.E.S.)

g) Development of an NO_x model. (Choquette)

IV. Environmental Impact

A. Aquatic Effects
- lake and stream chemistry
- lake, stream and sediment biology

a) Develop an inventory (Canada or continental) of
1) water chemistry data
2) fish or aquatic population data. (A.E.S.)

b) It appears that adverse effects on organisms depend on chemical species (i.e. SO_2, SO_4, SO_3, etc.). Measurement program at 2 calibrated watersheds to determine S, N speciation in precipitation. (A.E.S.)

c) The amount of neutralizing material required to maintain lake pH and buffering capacity at desirable levels for a given period of time.

B. Terrestrial Effects
- physics and chemistry of soil
- biosphere of vegetation existing on top of and within soils

a) Effect of acid rain on managed soil systems (i.e. agricultural soils, soils used in septic systems, etc.). (D. Jeffries)

b) Develop an inventory (Canada or continental) of terrestrial productivity data related to air damage (agricultural, i.e. white bean, and native, i.e. lichen populations). (A.E.S.)

c) Susceptibility geologically speaking
EMR's Uranium Reconnaissance Program
R.G. Skinner EMR
580 Booth Street (Johnson)

d) Influence of the terrestrial system (i.e. forest plus forest soil plus parent material) on precipitation chemistry.

i) Overall change in precipitation chemistry with passage through terrestrial system and the variation of this with watershed characteristics and loadings.

ii) Change in precipitation chemistry as throughfall, stemflow and the variation of this with forest conditions and loadings.

iii) Change in precipitation, throughfall and stemflow chemistry with passage through the forest floor, soil and parent material and the variation of this with soil conditions and loadings.

iv) Quantification of the role of the terrestrial system as a sink for air pollutants and the variation of this with system properties. (Sullivan)

e) Influence of acid precipitation on the terrestrial system.

i) Effect of acid loading on foliage chemistry and element turnover and ultimately upon growth.

ii) Influence of acid loading on soil chemical and biochemical properties and processes. (Sullivan)

V. Remedial Measures

A. Aquatic

a) Whether $CaCO_3$ alone is adequate as a neutralizing agent, and whether it alone will prevent initial destruction of phytoplankton and zooplankton populations.

b) Whether application to the lake surface is the best application technique or whether treatment of stream inflows and watershed soils is necessary for long-term improvements.

c) Whether any treatment will be effective enough to eliminate problems re large loads of acid at spring runoff.

d) Whether decrease of heavy metals in Sudbury area lakes and Al in other acidic lakes will be sufficient under any treatment conditions to make neutralization worthwhile.

e) Whether nutrient levels (particularly P) will be affected, and what effect this will have, if any, on primary production.

f) Whether zooplankton, benthos and invertebrate populations will recover to adequate species composition and biomass levels for oligotrophic lakes so that they will provide a food supply for fish populations.

g) Whether fish populations introduced into treated lakes that were very acidic will i) reproduce; ii) withstand metal levels, particularly Al, still present after treatment; iii) withstand spring pH depressions.

h) Whether existing fish populations in moderately acidic lakes will recover after treatment.

VI. Socio-economic Impact

a) Develop an Economic Impact Assessment relating L.R.T.A.P. effects and
   i) forest industry
   ii) fishing industry (anadromous)
   iii) tourism. (A.E.S.)

b) Socio-economic impact evaluation. (Jeffries)

c) Socio-economic policy framework for L.R.T.A.P. (Munn)

VII. Health Effects

VIII. Other

a) Develop an inventory (Canada or continental) of publications related to L.R.T.A.P. (A.E.S.)

b) A public information service with sufficient scientific validity that the "man-on the street" can understand the seriousness and complexity of the problem. (Jeffries)

APPENDIX THREE

ONTARIO POLLUTANT INVENTORY INFORMATION

T.S. Wong
Model Project Engineer
Air Quality and Meteorology Section
Air Resources Branch
Ontario Ministry of the Environment
April 1975

CONTENTS

		Page
1.	Introduction	1
2.	Classification of Sources	2
3.	Inventory Design	2
4.	Inventory Methodology	5
5.	Emission Calculation	9
6.	Data Management	13
7.	Information Update	15

APPENDIX

I	Questionnaire Forms
II	Formats of Inventory Reports and Summaries
III	Approvals Record for Emission Inventory Update, Form UP-12
IV	Examples of Emission Factors

INTRODUCTION

The Ontario Pollutant Inventory is an advanced computerized information system for the management of air pollution emission inventory for the Air Resources Branch, Ontario Ministry of the Environment.

The first source surveillance of air pollution in Ontario dated back to July 1969 when a detailed emission inventory was carried out for the Metropolitan Toronto Area. To date, the system has been expanded geographically throughout the province with complete inventories for Toronto, Hamilton and Niagara Peninsula. In addition, industrial emission inventories are available for Southeast, Northeast and Northwest regions. Steps are being taken to complete these partial inventories.

The Metro Toronto Inventory, containing 532 point sources and some 9,600 area source entries, required about 10,000 man-hours[1] for completion and is believed to be the most detailed and the most thorough inventory ever compiled for an urban region. With the experience gained in the Toronto inventory, the Hamilton inventory with 118 point sources and about 3,700 area source entries required less than 3,000 man-hours[1] for compilation.

Information available from the emission inventory includes source emissions, locations, magnitude, frequency, duration and the relative contribution of the emissions. Ideally, in the determination of emission quantities, field measurements or stack gas tests of all sources of interest would be necessary, but this is impractical because the emission inventory covers a large area with thousands of sources. Emissions can be estimated for sources without actual measurements by the use of emission factors. The emission factor is obtained by actual measurements, material balances and engineering estimates for a number of individual sources in a class and then a statistical average is applied to that class with respect to an emission index

such as fuel consumption or production rate.

Emission data generated from the system provides a variety of functions. It can be used in air pollution abatement programs, urban planning projections, in the design of sampling programs, in developing a control strategy, and, in conjunction with meteorological input, to predict present as well as future ambient air quality.

2. CLASSIFICATION OF SOURCES

Depending on the size of emission quantities, the Ontario Pollutant Inventory sources are classified into point source and area source. Point sources are the stationary sources that individually contribute significant quantities of pollutants, usually in excess of 100 lb/day. Typical of these are power plants, municipal incinerators, chemical process industries, steel mills, food and agricultural industries and petroleum refineries. Area sources are smaller sources that individually do not contribute significantly to the air pollution problem but their collective impact may be very significant. Examples are automobiles, shipping, railroads, aircraft, small combustion operations for space heating, small industries and small scale waste disposal.

At this time, fugitive dust sources are not included in the inventory. This type of source is commonly emitted from unpaved roads and streets, agriculture, construction sites, building demolition, quarrying, mining and materials storage piles. Its effect may be significant in some areas, and thus needs to be included in the emission data for air quality simulations.

3. INVENTORY DESIGN

A point source in the inventory is associated with detailed information relating to the plant, firm or enterprise.

It may contain a number of emission points associated with different activities and categories. In most cases, an emission point is the well-defined location where pollutants are emitted, through a stack or a physically bounded area.

Generally speaking, the point and area sources fall into the categories of:-

(1) Fuel combustion in stationary and mobile sources.

(2) Manufacturing processes.

(3) Waste disposal sources.

All the sources are properly identified according to the geographical location by using the Universal Transverse Mercator (UTM) grid system with a uniform size of 1 kilometer square. A point source is pinpointed to the definite grid location correct to 1/10 of a kilometer, then a serial number is added to complete the whole source number with 13 digits. For an area source, it is entered as a group source in the specific grid location, each with an 8-digit number identification.

General information for each point source includes source name, region and district designations, address and telephone number, person to contact about pollution control, nature of business of the source, number of employees, year of survey and the parent company name and address.

A very important use of the emission inventory is to provide input to the diffusion model to predict pollutant concentrations over small intervals of time and space. Variability of emission rates with respect to time has to be developed in the inventory to be compatible for this purpose. Detailed data showing the changing levels of activity on a seasonal, daily and hourly basis are required such as the

frequency variations for space heating on seasonal basis and the process and non-process operations based upon the days of the week and the number of shifts per day in operation. In the Ontario Pollutant Inventory, emission data are reported on an annual basis, i.e. lb/yr. In addition to time dependent variations, the pollutant release data is also required. This includes method of release, stack height, stack diameter, temperature and volume of the exit gas stream from the stack.

The inventory contains five major pollutants of primary importance. The general characteristics of these pollutants are described here; but more detailed information can be found in the US document[2].

Suspended Particulate -

This is the most visible of all air pollutants which is dispersed in the air either in solid or liquid phase and is within a certain size range usually less than 100 microns. Particulate air pollution may originate from many sources such as power generation, incineration, space heating, transportation, solid waste disposal, manufacturing and commercial operations. Particulates above certain concentration levels in a size less than 5 microns may cause injury to the human respiratory system and they can also combine with gaseous pollutants to form more adverse impact on human health and welfare.

Sulphur Dioxide -

A colourless, gaseous pollutant, arises mainly from the combustion of sulphur containing coal and fuel oils, and from industrial processes of petroleum refineries, sulphuric acid manufacture, iron and steel industry and refuse incineration. Adverse effects of sulphur dioxide pollution include irritation of respiratory system to human beings, acute or chronic leaf injury to plants and, with high particulate levels, cause of poor visibility and greater corrosion rate on materials.

Nitrogen Oxides (NO_x) -

Nitrogen oxide (NO) and nitrogen dioxide (NO_2) are generated by natural sources as well as man-made technological sources. NO_x levels in non-urban areas are low due to the natural scavenging processes. Emissions of technological NO_x may be from automobile exhaust, stationary combustion sources, incinerators and chemical processes. No evidence shows that NO has any adverse effects on health or welfare, however, by photochemical reactions, NO can be oxidized to NO_2, the only significant NO_x air pollutant. NO_2 causes toxic effect on the lungs and the reduction of visibility.

Hydrocarbons -

The hydrocarbons of concern in the inventory are those non-methane gas-phase hydrocarbons emitted into the atmosphere as contaminants by technological sources, such as the processing and use of petroleum products. Automobiles are the chief source in an urban area. No direct adverse effects from this class of pollution on human health have been shown, however, health effects attributed to photochemical smog are indirectly related to ambient levels of gaseous hydrocarbons.

Carbon Monoxide -

This is a colourless, odourless and toxic gas arising primarily from incomplete combustion of carbonaceous fuels. Automobiles contribute the largest quantity. Adverse effects on human health have been associated with the formation of blood carboxyhemoglobin, thus decreasing the oxygen carrying capacity of the blood and reducing the oxygen transfer to vital tissues.

4. INVENTORY METHODOLOGY

Depending on the accuracy of emission data required, several

inventory techniques are available for the collection of inventory data, namely use of published statistical data, rapid survey technique, comprehensive survey technique and the complex stack sampling procedure[3]. All these techniques have been employed in the Ontario Pollutant Inventory usually with some modifications. Generally, the simple techniques are used in area sources and the comprehensive survey technique for point sources.

Point Sources

A multi-page questionnaire was developed to delineate the point sources. The requisite information is collected by inspectors and engineers from the Regional Offices during their direct interviews. The establishments to be visited are identified by means of a manufacturing directory, fuel tax records, previous surveys, complaint history and inspectors' knowledge of their districts. The questionnaire forms are organized into:-

1. Fuel combustion.
2. Manufacturing activities.
3. Waste disposal.

Copies of these forms are included in Appendix I.

1. Fuel Combustion

Data is collected for all facilities that provide space and/or process heating by burning any kind of fuels such as coal, coke, wood, fuel oil, manufactured gas and natural gas. Large institutions such as universities and hospitals are in this category. Emissions from combustion are dependent not only on the fuel consumption quantities, but also on the type and size of combustion unit, the characteristics of fuel such as sulphur and ash contents as well as the operating conditions. Variations due to seasons, day of the week and diurnal factors determine the time dependency of the emissions.

2. Manufacturing Activities

This applies to all facilities that emit pollutants during the activities of manufacturing or product handling. The requisite information includes type of process, equipment capacity, principal product or raw material processed, annual production rate, control equipment and variation in activity level with respect to time. If emission data is available from stack sampling tests, this is included. Evaporation losses from petroleum tanks are also included in this category.

3. Waste Disposal

This category includes all solids and liquids whose disposal is capable of releasing air pollutants. Solid waste materials resulting from urban, industrial or commercial activities are usually burned in incinerators, for example, municipal incinerator. The requisite information is very similar to that in the manufacturing process. Control equipment is taken into account when emissions are estimated.

Area Sources[4]

Unlike point sources, area sources can hardly be surveyed individually by personal contact. Depending on the source type, either modified rapid survey or statistical data techniques can be used to derive the geographical emissions data.

1. Automobiles

The vehicle mile average speed technique is used in the inventory to estimate the emissions from automobiles. The requisite information includes traffic counts and average road speed. There are six emission classes in the inventory system covering light-duty and heavy-duty vehicles of roadway types, highways, major arteries and

urban streets. Traffic counts can be obtained from traffic surveys conducted by the Ministry of Transportation and Communication or local traffic agencies. If this data is not available, fuel sales data are used to estimate the emissions.

2. Shipping

The vessel movement data method is used to obtain fuel consumption data. The requisite information includes the number and types of ships that visit the harbour, length of their stay and type of fuel used. This information is usually provided by the harbour commission or shipping agencies. Time dependent emissions are calculated for the underway and in-berth operations for a grid square.

3. Railroads

Contacts with railroad companies are used to collect information on trip frequency and fuel consumption figures. Estimation of emissions is based on the apportionment by miles of track per grid square and the freight yard operations.

4. Aircraft

Airport authorities are contacted for their records on landing and take-off frequency and the type of aircraft for each flight. Time and distances are developed for various phases of flight for up to 1,000 ft. altitude. On the basis of total number of flights, emissions are estimated and apportioned into each of the grid squares involved.

5. Small Industrial and Commercial Heating

City maps are used to locate large buildings and small industrial companies. Fuel data is collected by telephone contacts. Estimated emissions are entered in the specific grid squares.

6. Residential Heating

Published data technique is applied in this category. Gas and

oil sales for an area together with the fuel characteristics are obtained from gas companies. The difference between the total fuel usage and that assigned to other categories is assigned to this type of space heating. Information on land use and population distribution is collected to apportion the fuel consumption rates by grid square. Statistical sampling of the residential fuel usage can be employed to improve the accuracy of this technique.

5. EMISSIONS CALCULATION

The requisite information collected is forwarded to the Air Resources Branch for inventory processing. The data are carefully checked and reviewed for validity and accuracy. Emissions are calculated by using the appropriate emission factors either by hand or by computer. It should be emphasized that the use of actual field measurements will override that of emission factors obtained from literature.

Emission factors are available from Compilation of Air Pollutant Emission Factors. The basic data collected in the surveys are first compared in detail with those in the literature; then, realistic emission estimates are derived by applying engineering knowledge and judgement to the type of technology, fuel, and operating and maintenance conditions of the source concerned. Utilization of emission factors is illustrated as follows:-

Fuel Combustion - Coal

Given:

Quantity per year = 10,000 tons

Sulphur content, S = 2.5%

Ash content, A = 10%

Combustion equipment: spreader stoker without fly ash reinjection

Control equipment: multiple cyclones

Estimated collection efficiency = 85%

From emission factor table:

Particulates = 13A lb/ton of coal

Therefore,

$$\text{Particulate emissions} = \left|(13)\ (10)\ \frac{\text{lb of Pa}}{\text{ton of coal}}\right| \left|\frac{10{,}000 \text{ tons of coal}}{\text{year}}\right| \left|1 - 0.85\right|$$

$$= 195{,}000\ \frac{\text{lb of Pa}}{\text{year}}$$

Sulphur dioxide = 38S lb/ton of coal

Therefore,

$$SO_2 \text{ emission} = \left|(38)\ (2.5)\ \frac{\text{lb of } SO_2}{\text{ton of coal}}\right| \left|\frac{10{,}000 \text{ tons of coal}}{\text{year}}\right|$$

$$= 950{,}000\ \frac{\text{lb of } SO_2}{\text{year}}$$

Nitrogen oxides = 15 lb/ton of coal

Therefore,

$$NO_x \text{ emission} = \left|\frac{15 \text{ lb of } NO_x}{\text{ton of coal}}\right| \left|\frac{10{,}000 \text{ tons of coal}}{\text{year}}\right|$$

$$= 150{,}000\ \frac{\text{lb of } NO_x}{\text{year}}$$

Carbon monoxide = 2 lb/ton of coal

Therefore,

$$\text{CO emission} = \left[\frac{2 \text{ lb of CO}}{\text{ton of coal}}\right]\left[\frac{10{,}000 \text{ tons of coal}}{\text{year}}\right]$$

$$= 20{,}000 \frac{\text{lb of CO}}{\text{year}}$$

Hydrocarbons = 1 lb/ton of coal

Therefore,

$$\text{HC emission} = \left[\frac{1 \text{ lb of HC}}{\text{ton of coal}}\right]\left[\frac{10{,}000 \text{ tons of coal}}{\text{year}}\right]$$

$$= 10{,}000 \text{ lb of HC/yr}$$

Manufacturing Activities - Pig Iron Manufacturing in Blast Furnace.

Given:

Quantity per year = 1,000,000 tons of pig iron

Control equipment = none

The furnace was installed two years ago.

Emission Factor Table shows:-

	Total Particulates	Carbon Monoxide
Total uncontrolled	lb/ton 150	lb/ton 1750
	(130 to 200)	(1400 to 2100)

New furnace with good operating and maintenance conditions suggests the use of lowest emission factors for the unit.

Therefore,

$$\text{Particulate emission} = 130 \frac{\text{lb}}{\text{ton}} \times 1{,}000{,}000 \frac{\text{ton}}{\text{year}}$$

$$= 130{,}000{,}000 \text{ lb/yr}$$

$$\text{Carbon MOnoxide emission} = 1400 \frac{\text{lb}}{\text{ton}} \times 1{,}000{,}000 \frac{\text{ton}}{\text{year}}$$

$$= 1{,}400{,}000{,}000 \frac{\text{lb}}{\text{year}}$$

Waste Disposal - Incineration

Given:

Method of disposal - Commercial operation burning

Quantity per year = 1,000 tons of refuse

Type of incinerator: multiple chamber

From Emission Factor Table:-

$$\text{Particulate emission} = 7 \frac{\text{lb}}{\text{ton}} \times 1{,}000 \frac{\text{tons}}{\text{year}}$$

$$= 7{,}000 \text{ lb/yr}$$

$$SO_2 \text{ emission} = 1.5 \frac{\text{lb}}{\text{ton}} \times 1{,}000 \frac{\text{tons}}{\text{year}}$$

$$= 1{,}500 \text{ lb/yr}$$

$$NO_x \text{ emission} = 3.0 \frac{\text{lb}}{\text{ton}} \times 1{,}000 \frac{\text{tons}}{\text{year}}$$

$$= 3{,}000 \text{ lb/yr}$$

$$CO \text{ emission} = 10 \frac{\text{lb}}{\text{ton}} \times 1{,}000 \frac{\text{tons}}{\text{year}}$$

$$= 10{,}000 \text{ lb/year}$$

$$\text{HC emission} = 3 \frac{\text{lb}}{\text{ton}} \times 1{,}000 \frac{\text{tons}}{\text{year}}$$

$$= 3{,}000 \text{ lb/year}$$

6. DATA MANAGEMENT

After the information data have been checked, calculations been performed, if necessary, such data are coded in the keypunch formats by the model personnel and sent to computer centre for data processing. An Emission Inventory Master File of both point and area sources is thus created on magnetic tape which is arranged in order of source location in the UTM grid coordinates.

Reports and Summaries

Depending on the data needs of various degrees of detail, different reports and summaries are available from the system. These retrievals are listed below, their formats are shown in Appendix II.

Point source report and/or area source report are usually produced. The point source report contains all the technical details of sources. A single source may have a number of emission points which carry proper category identifications of fuel combustion, manufacturing activities or waste disposal.

The area source report shows, in every grid square, the source type and annual emission quantities of the five pollutants. The commonly used summaries and tabulations of emissions data are:-

(a) Emission Summary by pollutant for a region, listing categories of sources, their total contribution and percentage of each of the five pollutants in the region.

(b) Size of contribution, which summarizes emission quantity of each of the five pollutants for point sources and lists each source in order of its size of pollutant emission.

(c) Emission by Source Type, listing the point sources by process or combustion type. The sequence is by source name and the pollutant summaries are shown.

(d) Control Equipment Summary, listing sources by type of air pollution control equipment. The control equipment detail and emission data are shown.

(e) Cross Reference listing all point sources by:-

(i) Source name in alphabetical order.

(ii) Source address in alphabetical order.

(iii) Grid location in numerical order.

This list helps in locating sources on a map or in determining what sources are located in a specific area.

7. INFORMATION UPDATE

In order to keep the emission inventory current, sources must be continuously updated to reflect changes in the environment. Plants may close, new facilities may commission, automobile exhausts will undergo control and other modifications may take place. Information about new sources or modifications of existing sources of emissions are supplied to the Air Resources Branch by the Approvals personnel through approval application notice. A form known as UP-12 serves for this purpose and is shown in Appendix III. Other changes such as fuel switch or modification of manufacturing process are usually recorded in periodic source resurveys. The resurveys are scheduled on a continuous basis to avoid large workload bulge. Depending on the size of emission quantities, a source is resurveyed at either one or two year intervals. Due to the large number of sources to be updated every month, computer update preparation is being developed. However, the resurvey interviews are carried out by the Regional Officers.

REFERENCES

1. L. Shenfeld and A.E. Boyer, "The Utilization of an Urban Air Pollution Model in Air Management", Ontario Ministry of the Environment, 1972.

2. Air Quality Criteria for Particulate Matter (AP-49), Sulphur Dioxide (AP-50), Nitrogen Oxides (AP-84), Hydrocarbons (AP-64) and Carbon Monoxide (AP-62), US EPA.

3. R.A. Deininger, "Design of Environmental Information", Ann Arbor Science, 1974.

4. Ontario Air Quality Model Information

APPENDIX I

QUESTIONNAIRE FORMS

(PLEASE PRINT ALL INFORMATION)

(1) REGION ☐ DISTRICT ☐☐

(2) SOURCE NUMBER ☐☐ ☐☐☐ ☐☐ ☐☐☐ ☐☐☐

ONTARIO EMISSION INVENTORY
INTERVIEW QUESTIONNAIRE FORM

Data Compiled by: ____________ Date: ______
Updated by: ____________ Date: ______
Coded by: ____________ Date: ______

(3) SOURCE NAME: ____________
(4) ADDRESS: ____________
(5) CITY/POSTAL CODE: ____________
(6) CONTACT: ____________
(7) AREA CODE - TELEPHONE: ____________
(8) COMPANY NAME: ____________
(9) ADDRESS: ____________
(10) CITY/PROVINCE: ____________
(11) NATURE OF BUSINESS: ____________

(12) SOURCE CODE: ______ (13A) NO. OF EMPLOYEES ______ (14A) YEAR OF SURVEY ______ (14B) UPDATED: 1. ______ 2. ______ 3. ______

From: ______ To: ______

(13B) FLOOR AREA: ______ Sq.Ft.

FOR USE BY MODEL CODING STAFF ONLY:

SOURCE NAME ☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐

ADDRESS ☐☐☐☐ ☐☐☐☐☐☐☐☐☐ ☐☐ ☐

CITY/POSTAL CODE ☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐

CONTACT ☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐

AREA CODE - TELEPHONE ☐☐☐ ☐☐☐ ☐☐☐☐

COMPANY NAME ☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐

ADDRESS ☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐

CITY/PROVINCE ☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐

SOURCE CODE ☐☐☐☐ NO. OF EMPLOYEES ☐☐☐☐

YEAR OF SURVEY ☐☐

NATURE OF BUSINESS ☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐
☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐

FIRST UPDATE ☐☐ SECOND UPDATE ☐☐ THIRD UPDATE ☐☐

November 2/72

FUEL COMBUSION (Process and Space Heating) (17) Source Name_____

(18) Number of Boilers/Stack_____ (19) Emission Point Number ☐☐☐

(20) Boiler Number	(21) Rated Fuel Input	(22) Fuel Used	(23) Combustion Equipment

Operating Data for Boilers:

(24) Supplier of and type of fuel used_____

(25) Length of interruptible gas period, days (a) Contract:_____(b)Actual_____
(26) Quantity per year (MCF, IMP. GAL. TON)_____
(27) Seasonal variation percent of annual_____
(28) Day-to day variation, days in operation/wk_____
(29) Diurnal variation, by hours per day_____

(30) Sulphur content, percent as received_____Avg._____Max.
(31) Ash content, percent as received_____Avg._____Max.
(32) Heat content HHV (BTU as received/CF, IMP. GAL., LB)
_____Avg._____Min.

(33) Use of Fuel:

Space heating, percent_____
Process heat, percent_____
Other (specify), percent_____

FOR OFFICE USE ONLY:

Fuel code ☐☐ Sulphur Content (%) ☐☐ Ash Content (%) ☐☐

Fuel Quantity/yr ☐☐☐☐☐☐☐☐ MCF, IMP.GAL, TON Interruptible Gas (Y,N or A) ☐ Interruptible Period (days) ☐☐☐

Coal Combusion Equipment Code ☐☐ Space Heating (%) ☐☐☐ Cross Reference ☐☐☐

Seasonal Variation % ☐☐☐☐☐☐

Day of week Variation Code ☐☐

Diurnal Variation COde ☐☐

3.

FUEL COMBUSION (cont'd)

Source name__________
Emission Point Number [| |]

Air Pollution Control Equipment:

(34) Type__________
(35) Collection Efficiency, percent Design__________
Estimated__________
(36) Year Installed__________
(37) Condition__________

Stack Data:
(38) Method of release__________
(39) Stack height (above grade), ft.__________
(40) Stack diameter (inside, top), ft.__________
(41) Material of construction__________
(42) Exit gas temperature, °F.-Top:__________Avg.__________Max.
Bottom :__________Avg.__________Max.
(43) Excess air, percent__________Avg.__________Min.
(44) Exit gas volume (at exit temp.) CFM__________

Emission Data:

Estimate of Emissions by the Company - or summarize results of calculations on estimations and show source of reference.

(45) Type	(46) Quantity, lb/yr	(47) Basis

FOR OFFICE USE ONLY:
Air Pollution Control equipment

Collection Efficienty (designed) % [| .]

Type Code [| |]

Collection Efficiency (estimated) % [| .]

Year Installed [|]

Condition [| | | | | | | | | | | | | | | | | | |]

Release Data
Method of Release [|] Stack Height (ft) [| | |] Stack Dia. (ft) [| .]

Exit gas temp. (°F) [| | |] Excess Air (%) [| |] Exit Gas Vol. (CFM or code) [| | | | | | | |]

Calculated Emissions
Emission Factor Code [|] SO_2 (lb/yr) [| | | | | | | |] NO_x (lb/yr) [| | | | | | | |]

Particulates (lb/yr) [| | | | | | | |] CO lb/yr [| | | | | | | |] Hydrocarbons (lb/yr) [| | | | | | | |]

Other Pollutants (coded) [| | | |] [| | | |]

Remarks (only by Model Staff)

[| | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |]

Source Name _____

Emission Point Number: ☐☐☐

MANUFACTURING ACTIVITIES (See also Summary Sheet P.11)

(48) Process Name or Product Description _____

_____

(49) Equipment Type _____

_____

(50) Equipment Capacity _____

(51) Principal Product or Raw Material _____

(52) Quantity per year _____

(53) Unit of Measurement _____

(54) Seasonal variations, % of annual _____ / _____ / _____ / _____

(55) Day-to-day variation, days in operation/week _____

(56) Diurnal variation, hr./day _____

==========

FOR OFFICE USE ONLY:

Process Data

Process Name ☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐

Equipment Capacity ☐☐☐☐☐☐☐☐☐☐

Principal Product or Raw Material ☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐

Quantity/yr ☐☐☐☐☐☐ Unit of Measurement ☐☐☐

Remarks (only by Model Staff)

☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐

Variation

Seasonal Variation (%) ☐☐☐☐☐☐☐

Day-of-week Variation (code) ☐☐

Diurnal Variation (code) ☐☐

5.

MANUFACTURING ACTIVITIES (cont'd)

SOURCE NAME _____

Emission Point No. [ ]

AIR POLLUTION CONTROL EQUIPMENT:

(57) TYPE _____

(58) Collection Efficiency, percent Design _____
Estimated _____

(59) Year Installed _____

(60) Condition _____

STACK DATA (list by Equipment Served) :

(61) Method of release _____

(62) Stack height (above grade), ft _____

(63) Stack diameter, inside top, ft. _____

(64) Material of construction _____

(65) Exit gas temperature, °F - Top: _____ Bottom: _____

(66) Exit gas volume (at exit temp.), CFM _____

EMISSION DATA:

ESTIMATE OF EMISSIONS BY THE SOURCE: (or summarize results of calculations or estimation and show source of reference)

(67) Type	(68) Quantity, lb/yr	(69) Basis

FOR OFFICE USE ONLY:

AIR POLLUTION CONTROL EQUIPMENT

Type Code [ ]

Year Installed [ ]

Collection Efficiency (designed) [ ] %

Collection Efficiency (estimated) [ ] %

Condition [ ]

RELEASE DATA

Method of Release [ ]

Stack Height (ft) [ ]

Stack Dia. (ft) [ ]

Exit gas temp. top (F) [ ]

Exit Gas Vol (CFM or code [ ]

CALCULATED EMISSIONS

Emission Factor Code [ ]

SO_2 (lb/yr) [ ]

NO_x (lb/yr) [ ]

Particulates (lb/yr) [ ]

CO lb/yr [ ]

Hydrocarbons (lb/yr) [ ]

Other Pollutants (coded) [ ] [ ]

6.

Source Name ____________________

Emission Point Number: [| | |]

WASTE DISPOSAL (Solids and Liquids whose disposal is capable of releasing Air Pollutants)

(70) Method of Disposal ____________________

(71) Description of Waste disposed of ____________________

(72) Waste Type or Percent of Total that is Combustible __________
(73) Heating Value (BTU's/lb.) __________
(74) Moisture Percent __________
(75) Ash Percent __________
(76) Quantity in Tons per year __________
(77) Seasonal variation, % of annual __________
(78) Day-to-day variation , days in operation/week __________
(79) Diurnal variation, by hr./day __________

(80) Type of Incinerator __________
(81) Rated capacity lb/hr. __________
(82) Auxiliary Fuel used __________

= =

FOR OFFICE USE ONLY:

Disposal Data

Type of Waste. [| | | | | | | | | | | | | | | | | | | |]

Method of Disposal. [| | | | | | | | | | | | | | | | | | | |]

Quantity/yr. [| | | | | |] Unit of Measure. [| |] Combustible %. [|]

Heating Value (Btu's/lb.) [| | | |] Moisture %. [| |] Ash %. [|]

Remarks (only by Model Staff)

[| | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |]

Seasonal Variation. [| | | | | | |]
1 2 3 4

Day-of-week Variation (Coded) [|]

Diurnal Variation(coded). [|]

7

Source Name _____

WASTE DISPOSAL (cont'd)

Emission Point Number [ ][ ][ ]

AIR POLLUTION CONTROL EQUIPMENT:

(84) Type _____

(85) a. Year Installed _____

b. Condition _____

(86) Collection Efficiency, % Design _____

Estimated _____

STACK DATA (list by Equipment served):

(87) Stack height, ft. _____

(88) Method of release _____

(89) Stack diameter, inside top, ft. _____

(90) Material of construction _____

(91) Exit gas temperature °F. - Top: _____ Bottom: _____

(92) Exit gas volume, (at exit temp.), CFM _____

(93) Excess air _____

ESTIMATE OF EMISSIONS BY THE SOURCE: (or summarize results of calculations or estimations and show source of reference)

(94) Type	(95) Quantity, lb/yr	(96) Basis

==========

FOR OFFICE USE ONLY:

AIR POLLUTION CONTROL EQUIPMENT

Type Code [ ][ ][ ] Collection Efficiency (designed) % [ ][ ].[ ]

Year Installed [ ][ ] Collection Efficiency (estimated) % [ ][ ].[ ]

Condition [ ][ ][ ][ ][ ][ ][ ][ ][ ][ ][ ][ ][ ][ ][ ]

RELEASE DATA

Method of Release [ ][ ] Stack Height (ft) [ ][ ][ ][ ] Stack Dia. (ft) [ ][ ].[ ]

Exit gas temp. (°F) [ ][ ][ ][ ] Excess Air % [ ][ ][ ] Exit Gas Vol. (CFM or code) [ ][ ][ ][ ][ ][ ][ ]

CALCULATED EMISSIONS

Emission Factor Code [ ][ ] SO_2 (lb/yr) [ ][ ][ ][ ][ ][ ][ ][ ] NO_x (lb/yr) [ ][ ][ ][ ][ ][ ][ ][ ]

Particulates (lb/yr) [ ][ ][ ][ ][ ][ ][ ][ ] CO lb/yr [ ][ ][ ][ ][ ][ ][ ][ ][ ] Hydro-carbons (lb/yr) [ ][ ][ ][ ][ ][ ][ ][ ]

Other Pollutants (coded) [ ][ ][ ][ ][ ] [ ][ ][ ][ ][ ]

APPENDIX II

FORMATS OF INVENTORY REPORTS AND SUMMARIES

ONTARIO POINT SOURCE EMISSION REPORT JAN 27, 1975 Regular Gas Co. PAGE 01 GRID-SERIAL 0?646-47553-C01
REGION 1 DISTRICT AB AIR MANAGEMENT BRANCH .. MINISTRY OF THE ENVIRONMENT

SOURCE NAME	Regular Gas Co.	COMPANY NAME	UNK	SOURCE CODE	3690
ADDRESS	1234 UNAVAIL ST E	ADDRESS	1234 UNAVAIL ST E	SOURCE DESC.	PETROLEUM PROD. IND.
CITY-ZONE	SARNIA ONTARIO	CITY-PROVINCE	SARNIA ONTARIO	NO. OF EMPLOYEES	0
CONTACT	U.K.KNOWN			YEAR OF SURVEY	1973
TELEPHONE	123-456-7895			FIRST UPDATE	19
NATURE OF BUSINESS	PETRO-CHEMICAL			SECOND UPDATE	19
				THIRD UPDATE	19

EMISSION POINT NUMBER 001 FUEL COMBUSTION .. NOT INTERRUPTIBLE
FUEL 08 FUEL OIL6 1.30 % SULPHUR % ASH INTERRUPTIBLE PERIOD DAYS CROSS REFERENCE POINT
ANNUAL FUEL QUANTITY 572,200 IMPGAL SPACE HEATING 98%
SEASONAL VARIATION 40-10-10-40 DAY-OF-WEEK 01 DIURNAL 08

CONTROL EQUIPMENT	.RELEASE METHOD 01	.CALCULATED EMISSIONS -COMPUTED CODE 01
COLLECTION EFFICIENCY	. BRICK STACK	. SO2 139,845 LB/YR
DESIGNED	. STACK HT. 130	. NOX 54,931 LB/YR
ESTIMATED	. STACK DIA 6.0	. PARTICULATES 15,792 LB/YR
INSTALLED	. EXIT TEMP 375 F	. CO 137 LB/YR
CONDITION	. EXCESS AIR 20 %	. HYDROCARBONS 2,059 LB/YR
	. EGV C 4013 CFM	. OTHERS PRESENT -
REMARKS		

EMISSION POINT NUMBER 002 MANUFACTURING PROCESS .. F C CRACKING UNIT EQUIPMENT CAPACITY 16000 B/D
PRINCIPAL PRODUCT OR RAW MATERIAL FRESH FEED QUANT/YEAR 5,840,000 BBL
SEASONAL VARIATION 25-25-25-25 DAY-OF-WEEK 01 DIURNAL 03

CONTROL EQUIPMENT 003 MLTPL CYCLON	.RELEASE METHOD 02	.CALCULATED EMISSIONS -MANUAL CODE 00
COLLECTION EFFICIENCY	. STEEL STACK	. SO2 2,879,120 LB/YR
DESIGNED	. STACK HT. 250	. NOX 414,640 LB/YR
ESTIMATED 99.9%	. STACK DIA 10.7	. PARTICULATES 876,000 LB/YR
INSTALLED 1967	. EXIT TEMP 540 F	. CO LB/YR
CONDITION		. HYDROCARBONS 1,234,800 LB/YR
GOOD--CO BOILER	. EGV C 10 CFM	. OTHERS PRESENT -
REMARKS		

EMISSION POINT NUMBER 003 WASTE DISPOSAL .. TYPE VAR.SOLID IND.WASTES METHOD THERMAL OXIDATION
QUANTITY 1200 TON COMBUSTIBLE PERCENT 90 HEATING VALUE 6500 BTU/LB. MOISTURE PERCENT 25.0 ASH PERCENT 10
SEASONAL VARIATION 25-25-25-25 DAY-OF-WEEK 02 DIURNAL 01

CONTROL EQUIPMENT	.RELEASE METHOD 99	.CALCULATED EMISSIONS -MANUAL CODE 95
COLLECTION EFFICIENCY	.	. SO2 24,000 LB/YR
DESIGNED	. STACK HT. 20	. NOX 60,000 LB/YR
ESTIMATED	. STACK DIA 40.0	. PARTICULATES 240,000 LB/YR
INSTALLED	. EXIT TEMP 700 F	. CO 720,000 LB/YR
CONDITION	. EXCESS AIR 80 %	. HYDROCARBONS 240,000 LB/YR
	. EGV C 10 CFM	. OTHERS PRESENT -
REMARKS OPEN PIT INCINERATOR		

ONTARIO AREA SOURCE EMISSION REPORT APR 07, 1975 GRID SQUARE NUMBER 0614-4837

ENTRY NO.	EMISSION CLASS DESCRIPTION	QUANTITY FACTOR	DIUR FACT	EMISSIONS - LBS/YEAR					
48	RESIDENTIAL - OIL OIL RESIDENTIAL HEATING	49000 .50	09	CALC SO2	4,165	PART CO	588 294	HC NOX	176 705
49	RESIDENTIAL - GAS GAS RESIDENTIAL HEATING	23760	09	CALC SO2	14	PART CO	451 475	HC NOX	190 1,188
78	COM PUB BLDG GAS COMMERCIAL GAS	80872	09	CALC SO2	48	PART CO	1,536 1,617	HC NOX	646 8,087
80	MAJOR HIGHWAY HWY 401 04	75000 .5	13	CALC SO2	8,212	PART CO	10,950 940,331	HC NOX	186,150 150,562
81	OTHER HIGHWAY HWY 27 DIXON 12	26300 .7	14	CALC SO2	4,031	PART CO	5,375 552,355	HC NOX	91,387 73,916
82	RESIDENTIAL STREET	2000 1.7	16	CALC SO2	744	PART CO	992 194,712	HC NOX	22,213 13,651
83	MAJOR ARTERY DIXON HWY 27 02	6000 .2	15	CALC SO2	262	PART CO	350 54,005	HC NOX	7,533 4,818
93	COM PUB BLDG DISTGTL COMM OIL LGT-REV	203053 .50	09	CALC SO2	17,259	PART CO	3,654 48	HC NOX	730 19,493

TOTAL SO2 :	34,735
PART;	23,896
HC :	309,025
CO :	1,743,837
NOX :	272,420

VERSION-AUG.74

AIR QUALITY MODEL FOR METROPOLITAN TORONTO

EMISSION SUMMARY - BY POLLUTANT M/F:10231 (TORONTO) RUN DATE SEPT 12, 74

(PERCENTAGE FIGURES SHOWN IN BRACKETS REFER TO CONTRIBUTION OF EACH SOURCE TYPE TO A SPECIFIC POLLUTANT)

MILLIONS OF LBS. EMITTED PER YEAR; IN BRACKETS: PERCENTAGE OF TOTAL

SOURCE TYPE	SO2	PARTICULATE	NOX	CO	HC	TOTAL
R.L.HEARN G.S.	32.33(7.17)	0.73(1.70)	14.43(6.93)	0.34(0.04)	1.58(0.94)	
LAKEVIEW G.S.	349.14(77.46)	6.65(15.52)	69.05(33.18)	3.82(0.50)	1.15(0.68)	
MUNCIPAL INCINERATORS	0.41(0.09)	9.10(21.24)	1.03(0.49)	2.49(0.32)	0.12(0.07)	
INDUSTRIAL SOURCES	15.21(3.37)	7.51(17.53)	19.54(9.38)	4.05(0.53)	43.88(26.13)	
AUTOS	3.93(0.87)	5.24(12.23)	72.14(34.66)	740.64(97.66)	105.99(63.13)	
RAILROADS	0.43(0.09)	1.08(2.52)	2.18(1.04)	0.58(0.07)	1.33(0.79)	
SHIPPING	0.89(0.19)	0.40(0.93)	0.66(0.31)	0.24(0.03)	0.31(0.18)	
AIRCRAFT	0.24(0.05)	1.17(2.73)	1.13(0.54)	2.20(0.29)	10.61(6.31)	
HEATING - RESIDENTIAL	17.98(3.97)	2.99(6.98)	4.27(2.05)	1.75(0.23)	0.95(0.56)	
HEATING - APARTMENTS	5.98(1.32)	2.14(4.99)	5.83(2.80)	0.22(0.02)	0.47(0.27)	
HEATING-SCHOOLS & UNIV.	5.72(1.26)	0.63(1.47)	2.86(1.37)	0.03(0.00)	0.17(0.10)	
HEATING-PUBL.COM.BLDGS	12.42(2.75)	2.90(6.77)	11.46(5.50)	0.40(0.05)	0.54(0.32)	
SMALL INDUSTRIES	5.99(1.32)	0.85(1.98)	2.72(1.30)	0.03(0.00)	0.10(0.05)	
INCINERATION: APARTMENTS, SCHOOLS, SMALL INDUSTRIAL, PUBL. AND COMMERCIAL BUILDINGS	0.10(0.02)	1.44(3.36)	0.80(0.38)	1.55(0.20)	0.69(0.41)	
TOTAL	450.71(27.68)	42.83(2.63)	208.10(12.78)	758.34(46.58)	167.89(10.31)	1627.87

TOTAL EMISSION LBS/YR	SOURCE NAME ADDRESS	GRID SERIAL REG-DIST	POINT EMISSIONS POINT NO.	QUANT.LBS/YR	TYPE
			004 -	648	
			005 -	900	
			006 -	648	
6,240 LBS.	PARLIAMENT HILL E BK PARLIMENT	04454 50301 REG 5 DIST	001 -	6,240	
4,933 LBS.	ST JOSEPHS HOSPITAL 384 ROGERS ST	02349 49092 REG 5 DIST AB	001 -	1,260	
			002 -	2,520	
			003 -	1,153	
4,218 LBS.	CORNWALL GENL.HOSP'L 510 SECOND ST E	05222 49852 REG 5 DIST CW	001 -	1,512	
			002 -	2,674	
			003 -	32	
2,895 LBS.	PETERBORO CIVIC HOSP KELLER ST	02315 49085 REG 5 DIST AB	001 -	1,080	
			002 -	915	
			003 -	900	
2,433 LBS.	OTTAWA GENL.HOSPITAL 43 BRUYERE ST	04454 50310 REG 5 DIST CO	001 -	2,433	
1,250 LBS.	HOTEL DIEU HOSPITAL 840 MCCONNEL ST N	05222 49861 REG 5 DIST CW	001 -	682	
			002 -	219	
			003 -	329	
522 LBS.	MCCORDUFFE ISOLAB MCCORDUFFE AV	04420 50190 REG 5 DIST	001 -	504	
			002 -	18	

BATH EMISSION QUANTITY BY SOURCE TYPE .. JAN 29, 1975 PAGE 4
FUEL COMBUSTION - CODE 04 NO.2 OIL

SOURCE NAME / ADDRESS	GRID-SERIAL REGION-DIST	EMISSION POINT	CONTROL EQUIPMENT	TOTAL EMISSIONS LBS/YR					OTHER POLLUTANTS		
ROCKCLIFFE C.F.B.	04495-50341-001 REG 5 DIST	013		SO2 1,020	PART 216	HC 43			0	0	
				CO 2	NOX 1,152						
ROCKCLIFFE C.F.B.	04495-50341-001 REG 5 DIST	012		SO2 2,125	PART 450	HC 90			0	0	
				CO 6	NOX 2,400						
ST JOSEPHS HOSPITAL 384 ROGERS ST	02349-49092-001 REG 5 DIST AB	003		SO2 3,596	PART 1,153	HC 230			0	0	
				CO 15	NOX 6,153						
UNION CARBIDE VISKIN 150 COLBORNE ST E	02014-49145-001 REG 5 DIST AL	004		SO2 2,264	PART 648	HC 129			0	0	
				CO 8	NOX 3,456						
UNION CARBIDE VISKIN 150 COLBORNE ST E	02014-49145-001 REG 5 DIST AL	002		SO2 4,780	PART 1,368	HC 273			0	0	
				CO 18	NOX 7,296						
UNION CARBIDE VISKIN 150 COLBORNE ST E	02014-49145-001 REG 5 DIST AL	006		SO2 2,264	PART 648	HC 129			0	0	
				CO 8	NOX 3,456						
UPLANDS C.F.B.	04479-50197-001 REG 5 DIST	003		SO2 3,060	PART 648	HC 129			0	0	
				CO 8	NOX 3,456						

SO2; 386,054PART; 58,311NOX ; 311,025CO ; 759HC : 11,644

TORONTO AIR POLLUTION CONTROL EQUIPMENT SUMMARY BY SOURCE CODE...FABRIC FILTER DEC 16, 1974 PAGE 008

SOURCE TYPE / SOURCE NAME / ADDRESS	EQUIPMENT CODE / EQUIPMENT CONDITION / PROCESS TYPE / YEAR INSTALLED	EFFICIENCY DES.	EFFICIENCY EST.	GRID-SERIAL NO. / ANNUAL QNTY / MATERIAL		EMISSIONS ANNUAL	EMISSIONS HOURLY (MAX. OPERATIONAL)
PLASTIC & RESIN MFRS	FABRIC FILTER	99.5	99.5	06481-48465-002	SO	LB/YR	LB/HR
BORDEN CHEMICAL	GOOD			4,216,580 LBS	CO	LB/YR	LB/HR
595 CORONATIO DR	PVC RESIN HANDLING			PVC RESIN	PA	21,083 LB/YR	2 LB/HR
WEST HILL SCARBORO	1966				NO	LB/YR	LB/HR
PAINT & VARNISH MFRS	FABRIC FILTER	90.0	90.0	06241-48395-001	SO	LB/YR	LB/HR
CANADIAN INDUSTR LTD	FAIR-GOOD			2,600 GAL	CO	LB/YR	LB/HR
1300 CASTLEFIE AV	SPRAY PAINTING			PAINT	PA	250 LB/YR	LB/HR
TORONTO 340					NO	LB/YR	LB/HR
PAINT & VARNISH MFRS	FABRIC FILTER		90.0	06177-48275-002	SO	LB/YR	LB/HR
CDN.PITTSBURGH IND.	FAIR			6,875 TON	CO	LB/YR	LB/HR
3730 LAKESHORE BL	PAINT MIXING			PAINT	PA	2,580 LB/YR	1 LB/HR
TORONTO 510	1965				NO	LB/YR	LB/HR
PAINT & VARNISH MFRS	FABRIC FILTER	99.0	92.0	06255-48336-001	SO	LB/YR	LB/HR
SHERWIN WILLIAMS CO.	NEW			2,600 TON	CO	LB/YR	LB/HR
263 SORAUREN AV	PAINT MANUFACTURE			PIGMENT	PA	366 LB/YR	LB/HR
TORONTO	1969				NO	LB/YR	LB/HR
SOAP MANUFACTURERS	FABRIC FILTER		99.0	06328-48344-004	SO	LB/YR	LB/HR
CANADA PACKERS LTD	GOOD			4,350 TON	CO	LB/YR	LB/HR
525 FRONT ST E	SOAP MFG-MIX EXT&PRC			SOAP	PA	43,500 LB/YR	25 LB/HR
TORONTO	1962				NO	LB/YR	LB/HR
SOAP MANUFACTURERS	FABRIC FILTER	99.9	99.9	06334-48353-002	SO	LB/YR	LB/HR
COLGATE-PALMOLIVE LD	EXCELLENT				CO	LB/YR	LB/HR
64 COLGATE AV	MANUFACTURING AREA			DETERGENT	PA	3,870 LB/YR	LB/HR
TORONTO 252					NO	LB/YR	LB/HR
SOAP MANUFACTURERS	FABRIC FILTER	99.9	99.9	06334-48353-002	SO	LB/YR	LB/HR
COLGATE-PALMOLIVE LD	EXCELLENT			28,000 TON	CO	LB/YR	LB/HR
64 COLGATE AV	BULK HANDLING			SODASHSULPHATESILICA	PA	7,740 LB/YR	1 LB/HR
TORONTO 252					NO	LB/YR	LB/HR
SOAP MANUFACTURERS	FABRIC FILTER		30.0	06329-48345-002	SO	42 LB/YR	LB/HR
LEVER BROTHERS LTD	GOOD			71,200 TON	CO	28 LB/YR	LB/HR
1 SUNLIGHT PK	COAL			COAL	PA	898 LB/YR	LB/HR
TORONTO	1950				NO	16,394 LB/YR	2 LB/HR
SOAP MANUFACTURERS	FABRIC FILTER	99.9	99.5	06329-48345-002	SO	LB/YR	LB/HR
LEVER BROTHERS LTD	GOOD			36,500 TON	CO	LB/YR	LB/HR
1 SUNLIGHT PK	DETERGENT TOWER			DETERGENT	PA	71,000 LB/YR	11 LB/HR
TORONTO	1950				NO	LB/YR	LB/HR

DEPT. OF THE ENVIRONMENT

AIR MANAGEMENT BRANCH

POINT SOURCES ARRANGED IN ORDER BY SOURCE NAME

30948363005	3C3	APARTMENT-279 SUITES	700	ONTARIO ST	TORONTO	
30948363006	3C3	APARTMENT-279 SUITES	730	ONTARIO ST	TORONTO	
21548365001	3W3	APARTMENT-304 SUITES	200	WOOLNER	TORONTO	
28348441001	3N1	APARTMENT-307 SUITES	4000	YONGE ST	TORONTO	
29148401002	3C1	APARTMENT-330 SUITES	33	HOLLY ST	TORONTO	
29148406001	3C1	APARTMENT-357 SUITES	66	BROADWAY	TORONTO	
30548354007	3C3	APARTMENT-771 SUITES	484	CHURCH ST	TORONTO	
31648347001	3C4	APARTMENT-903 SUITES	275	SHUTER ST	TORONTO	
21748387003	3W3	ARROW HART CAN.LTD.	81	INDUSTRY ST	TORONTO 337	
38948479003	3E2	ATLANTIC PACKAGING	111	PROGRESS AV	TORONTO-AGINCOUR	
30448338004	3C3	BANK OF NOVA SCOTIA	44	KING W	TORONTO 1	
26548425001	3N1	BAYCREST HOSPITAL	3560	BATHURST STREET	TORONTO DOWNSVI	
23248364003	3C2	BEEF TERMINAL LTD	2255	ST CLAIR AVE W	TORONTO 9	
18148472002	3W4	BELL CANADA	20	NORELCO DR	TORONTO WESTON	
21948308001	3W1	BISHOP BLDG MATL LTD	21	FLEECELINE RD	TORONTO 14	
30448364002	3C1	BLOORVIEW CHILDRENS	278	BLOOR ST E.	TORONTO	
48148465002	3E2	BORDEN CHEMICAL	595	CORONATION DR	WEST HILL SCARBO	
23648367002	3C2	BOTTING ASPHALT	2	UNION ST	TORONTO	
22848364002	3C2	BROCKVILLE CHEM IND		HARRIS ROAD	TORONTO 9	
40948515001	3E2	C P RAILWAY TOR YARD		AGINCOURT	TORONTO	
23748357002	3C2	CADET CLEANERS LTD	290	OLD WESTON RD	TORONTO 9	
20748288001	3W1	CAMPBELL SOUP CO LTD	60	BIRMINGHAM ST	TORONTO 14	
18348402001	3W3	CAN GYPSUM CO LTD	21	OAK ST	TORONTO	
27848324002	3C2	CAN NATIONAL EXHIB		EXHIBITION PARK	TORONTO	

NAME

DEPT. OF THE ENVIRONMENT

AIR MANAGEMENT BRANCH

POINT SOURCES ARRANGED IN ORDER BY SOURCE ADDRESS

1554845501	3W2	THISTLETOWN	1800	ISLINGTON AVE N	TORONTO THISTLETC
1654841100	3W2	PHOTO ENGRAVERS LTD	2250	ISLINGTON AVE N	TORONTO ONT
2624832201	3C2	APARTMENT-118 SUITES	109	JAMESON AVE	TORONTO
1994844301	3W4	APARTMENT 111 SUITES	2600	JANE	NORTH YORK
2074839500	3W4	APARTMENT 325 SUITES	1555	JANE ST	NORTH YORK
1994845100	3W4	APARTMENT 198 SUITES	2775	JANE ST	NORTH YORK
1994845100	3W4	APARTMENT 230 SUITES	2801	JANE ST	NORTH YORK
1954845800	3W4	APARTMENT 162 SUITES	4500	JANE ST	NORTH YORK
2014843500	3W4	APARTMENT 160 SUITES	2425	JANE STREET	NORTH YORK
2074839200	3W3	DOMINION CELLULOSE	1350	JANE STREET	TORONTO 15
3084835501	3C1	FOUR SEASONS HOTEL	415	JARVIS ST	TORONTO
2274840600	3W4	APARTMENT 187 SUITES	2050	KEELE	NORTH YORK
2184842200	3W4	DEPT OF HIGHWAYS		KEELE & 401 HWY	TORONTO DOWNSVIE
2184847701	3N1	GULF OIL CANADA LTD	3985	KEELE ST	DOWNSVIEW
2194845100	3W4	APARTMENT 206 SUITES	3460	KEELE ST	NORTH YORK
2174847800	3N1	TEXACO CANADA LTD	3999	KEELE ST.	TORONTO DOWNSVIE
2114848500	3W4	YORK UNIVERSITY CUB	4700	KEELE STREET	DOWNSVIEW
2254839501	3N1	NORTH WEST GENERAL	2175	KEELE STREET	TORONTO WILLOWDA
2254844200	3N1	CANADIAN FORCES BASE		KEELE/SHEPPARD	TORONTO DOWNSVIE
1434844100	3W4	APARTMENT 196 SUITES	121	KENDLETON DR	ETOBICOKE
3954842700	3E1	APARTMENT 184 SUITES	720	KENNEDY RD	SCARBOROUGH
3074833801	3C4	NATIONAL TRUST BLDG	21	KING ST EAST	TORONTO
3114833901	3C3	KING EDWARD SHERATON	37	KING ST EAST	TORONTO
2684832701	3C2	TOR CARPET MFG COLTD	1179	KING ST W	TORONTO

ADDRESS

DEPT. OF THE ENVIRONMENT

AIR MANAGEMENT BRANCH

POINT SOURCES ARRANGED IN ORDER BY GRID

0642948442001	3E1	APARTMENT 264 SUITES	3171	EGLINTON E	SCARBOROUGH
0642948442002	3E1	APARTMENT 161 SUITES	3161	EGLINTON E	SCARBOROUGH
0643348450001	3E1	APARTMENT 194 SUITES	215	MARKHAM RD	SCARBOROUGH
0643848445001	3E1	APARTMENT 220 SUITES	3400	EGLINTON AVE E	SCARBOROUGH
0643848467001	3E2	APARTMENT 213 SUITES	3847	LAWRENCE E	SCARBOROUGH
0644548467001	3E2	APARTMENT 221 SUITES	4010	LAWRENCE E	SCARBOROUGH
0644548467002	3E2	APARTMENT 141 SUITES	4000	LAWRENCE E	SCARBOROUGH
0645648517002	3E2	MILLER PAVING LTD	1136	SHEPPARD AVE E	TORONTO AGINCOU
0645748491001	3E2	SCARBOROUGH COLLEGE	1265	MILITARY TRAIL	TORONTO WEST HI
0645848514001	3E2	RAPONI EASTWOOD PAV		SHEPPARD &REPAC	TORONTO SCARBOR
0647148459001	3E2	ROHM AND HAAS CO.	2	MANSE RD	WEST HILL
0648148465002	3E2	BORDEN CHEMICAL	595	CORONATION DR	WEST HILL SCARB
0648248466001	3E2	MOBIL PAINT CO	645	CORONATION DR	EWEST HILL TORO
0649548488001	3E2	JOHNS-MANVILLE COLTD		PORT UNION RD	TORONTO SCARBOR

GRID

APPENDIX III

APPROVALS RECORD FOR EMISSION INVENTORY UPDATE, FORM UP-12

Ministry of the Environment
Ontario

AIR RESOURCES BRANCH
APPROVALS RECORD FOR
EMISSION INVENTORY UPDATE

FORM UP-12

Region ☐ District ☐☐ Date _____

Source/Company Name: _____

Address: _____

Contact: _____ Telephone: _____

Nature of Business: _____

Type of Equipment for Approval: _____

Combustion	Process	Incineration
☐ New	☐ New	☐ New
☐ Modification	☐ Modification	☐ Modification

General Description: _____

_____

Equipment Production or Feed Rate: _____ Quantity/yr: _____

Specify kind of product or feed _____

Control Equipment _____ Estimated Efficiency _____

PART A

Regional Office

Type of Application
☐ Simple, complete Part B
☐ Complex, forward to Environmental Approvals Branch

Application Attached Yes ☐ No ☐

Significant Pollutants (lb/hr)

SO_2 _____

Part _____

HC _____

NO_x _____

CO _____

Other _____

PART B

Environmental Approvals Branch

Application No: _____

Anticipated Completion Date: _____

Application Confirmation:
☐ Approved ☐ Cancelled ☐ Denied

Comments: _____

PART C

Air Resources Branch

New Source Logged: _____ Date: _____

Update Requested: _____ Date: _____

Date Completed: _____

PART D

Installation Check

Satisfactory ☐ Not operational ☐ Unsatisfactory ☐

Comments: _____

Inspected by: _____ Date: _____

Form Initiated By: _____ Date: _____

16-056 8/75

APPENDIX IV

EXAMPLES OF EMISSION FACTORS

FUEL COMBUSTION EMISSION FACTORS - POINT SOURCES

Fuel Code	Fuel	Coal Equipment	Units	Emissions lbs/Units Part.	SO_2	NO_x	CO	HC
01	Coal	Pulverized Gen.	Tons	16A(2)	38S(1)	18	1	0.3
		Pulverized - Dry Bottom	Tons	17A(2)	38S(1)	18	1	0.3
		Pulverized - Wet Bottom w/o Fly Ash Reinjection	Tons	13A(2)	38S(1)	30	1	0.3
		Pulverized - Wet Bottom with Fly Ash Reinjection	Tons	24A(2)	38S(1)	30	1	0.3
		Cyclone	Tons	2A(2)	38S(1)	55	1	0.3
		Spreader Stoker w/o Fly Ash Reinjection	Tons	13A(2)	38S(1)	15	2	1
		Spreader Stoker with Fly Ash Reinjection	Tons	20A(2)	38S(1)	15	2	1
		All Other Stokers	Tons	2A(2)	38S(1)	6	10	3
		Hand-Fired Equipment	Tons	20	38S(1)	3	90	20
02	Gas		MCF	0.018	0.0006	0.23	0.0004	0.04
03	No. 1 Oil		Imp.Gals	0.018	0.170S(1)	0.096	0.00024	0.0036
04	No. 2 Oil		Imp.Gals	0.018	0.170S(1)	0.096	0.00024	0.0036
05	No. 4 Oil		Imp.Gals	0.0276	0.188S(1)	0.096	0.00024	0.0036
06	No. 5 Lt.Oil		Imp.Gals	0.0276	0.188S(1)	0.096	0.00024	0.0036
07	No.5 Hvy.Oil		Imp.Gals	0.0276	0.188S(1)	0.096	0.00024	0.0036
08	No. 6 Oil		Imp.Gals	0.0276	0.188S(1)	0.096	0.00024	0.0036
09	No. 6C Oil		Imp.Gals	0.0276	0.188S(1)	0.096	0.00024	0.0036

(1) S = Percentage Sulphur Content

(2) A = Percentage Ash Content

Table 7.5-1. EMISSION FACTORS FOR IRON AND STEEL MILLS[a,b]
EMISSION FACTOR RATINGS: A (PARTICULATES AND CARBON MONOXIDE)
C (FLUORIDES)

Type of operation	Total particulates		Carbon monoxide		Fluorides[c,d]			
					Gaseous (HF)		Particulates (CaF_2)	
	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT
Pig iron production								
Blast furnaces[e]								
Ore charge, uncontrolled	110	55	1750 (1400 to 2100)	875 (700 to 1050)	–	–	–	–
Agglomerates charge, uncontrolled	40	20	–	–	–	–	–	–
Total, uncontrolled	150 (130 to 200)	75 (65 to 100)	1750 (1400 to 2100)	875 (700 to 1050)	–	–	–	–
Settling chamber or dry cyclone	60	30	–	–	–	–	–	–
Plus wet scrubber	15	7.5	–	–	–	–	–	–
Plus venturi or electrostatic precipitator	1.5	0.75	–	–	–	–	–	–
Sintering[f]								
Windbox, uncontrolled[g]	20	10	–	–	–	–	–	–
Dry cyclone	2.0	1.0	–	–	–	–	–	–
Dry cyclone plus electrostatic precipitator	1.0	0.5	–	–	–	–	–	–
Dry cyclone plus wet scrubber	0.04	0.02	–	–	–	–	–	–
Discharge, uncontrolled	22	11	44	22	–	–	–	–
Dry cyclone	[illegible]	1.1	44	22	–	–	–	–
Dry cyclone plus electrostatic precipitator	0.11	0.055	44	22	–	–	–	–
Steel production								
Open hearth[h]								
No oxygen lance, uncontrolled	8.3 (5.8 to 12.0)	4.15 (2.9 to 6.0)	–	–	0.100	0.05	0.030	0.015
Venturi scrubber	0.17	0.085	–	–	0.011	0.0055	0.0015	0.0008
Electrostatic precipitator	0.17	0.085	–	–	0.100	0.050	0.0006	0.0003
Oxygen lance, uncontrolled	17.4 (9.3 to 22.0)	8.7 (4.65 to 11.0)	–	–	0.100	0.050	0.030	0.015

Table 7.5-1 (continued). EMISSION FACTORS FOR IRON AND STEEL MILLS[a,b]
EMISSION FACTOR RATINGS: A (PARTICULATES AND CARBON MONOXIDE)
C (FLUORIDES)

EMISSION FACTOR CODES FOR - WASTE DISPOSAL(Incineration).

Section Number	Activity			Part.	SO_2	NO_x	CO	HC
	Incineration -							
91	Municipal	- lbs/Ton)		30.0	1.5	2.0	1.0	1.5
92	Ind. & Comm. S.C.	- lbs/Ton)		15.0	1.5	2.0	20.0	15.0
93	Ind. & Comm. M.C.	- lbs/Ton)		7.0	1.5	3.0	10.0	3.0
94	Flue-Fed	- lbs/Ton)	of Material Incinerated	30.0	0.5	3.0	20.0	15.0
95	Flue-Fed Afterburner	- lbs/Ton)		6.0	0.5	10.0	10.0	3.0
96	Open-Burning	- lbs/Ton)		20.0	2.0	5.0	60.0	20.0
97	Pathological	- lbs/Ton)		8.0	0.0	3.0	0.0	0.0

APPENDIX FOUR

CANADIAN INVENTORIES OF SOURCES AND EMISSIONS OF SULPHUR DIOXIDE AND NITROGEN OXIDES

LRTAP Related Inventory Data Currently Available

1. National inventory of man-made sources and emissions of sulphur dioxide and nitrogen oxides for the base year 1974. The point source data are available on a plant basis, the area source data on a census division basis.

2. Inventory of man-made emissions of sulphur dioxide and nitrogen oxides for Eastern Canada i.e. for the provinces east of Saskatchewan, apportioned to an 80 x 80 km grid. The emissions data are a mix consisting mostly of 1974 information and some 1978 information.

3. National inventory of natural sources and emissions of sulphur compounds on a census division basis.

LRTAP Related Inventory Data Available in 1980

1. National inventory of man-made sources and emissions of sulphur dioxide and nitrogen oxides for the base year 1976 (updates of item 1. above). From this information, inventories on a grid basis will be developed.

2. National inventory of natural sources and emissions of nitrogen compounds on a census division basis.

3. Projections to the year 2000 of national emissions of sulphur dioxide from the copper-nickel smelting industry and of sulphur dioxide and nitrogen oxides from the power generating sector.

For further information contact:

P.J. Choquette or Frank Vena,
Air Pollution Control Directorate,
Environment Canada,
Ottawa, Ontario.
K1A 1C8

Tel: 819-997-3352

APPENDIX FIVE

MATHEMATICAL MODELLING

Measurements of acid precipitation tell you how much is coming down. However, you cannot tell where the stuff is coming from. Mathematical modelling can help you to answer this question.

Models can quantify the relative impact of sources.

1) Short-term models (monthly averages).
2) Long-term models (averages over five years?).
   - probably easier to model but harder to verify with present data base.

Model Types

Eulerian: Can take care of complex chemistry but very time consuming.

Lagrangian: Less time consuming but can only handle linear scavenging. Results seem to be pretty good.

SPATIAL RESOLUTION
TEMPORAL RESOLUTION

$$\hat{C} = \hat{Q}\,\hat{f}(\vec{x}, \text{CHEMISTRY}) \quad \text{ETC}$$

$$\bar{C} + c' = (\bar{Q} + Q')(\bar{f} + f')$$

$$\bar{C} = \bar{Q}\bar{f} + \overline{Q'f'}$$

USUALLY NEGLECTED

LONG-RANGE TRANSPORT

$$\frac{dp}{dt} = -(\lambda_d + \lambda_w + k_t)p$$

$$C_{SO_2} = \frac{Qf}{2\pi r h u} \exp\left(-\frac{\alpha r}{u}\right)$$

$$SO_{2d} \simeq \frac{Q v_d}{u} \frac{r}{h} f_p$$

$$SO_{2w} = \frac{Q \lambda_w r}{u}$$

f_p = FRACTION OF FUMIGATION

SULPHATE CONCENTRATION

$$c_{SO_4} = \frac{3Qk_t}{4\pi r h u}\left[\frac{\exp\left(-\frac{\alpha r}{u}\right) - \exp\left(-\frac{\beta r}{u}\right)}{(\beta - \alpha)}\right]$$

$$c_{SO_4}(MAX) = \frac{3Qk_t}{4\pi h u^2}$$

$$\approx 5\ \mu g\, m^{-3}$$

$$pH \sim 4.47$$

CONCLUSIONS FROM SIMPLE MODEL

1) LESS THAN 1% OF Q IS DEPOSITED AS SULPHATE WITHIN 50 KM OF SUDBURY

2) ~10% SO_2 DRY DEPOSITED WITHIN 100 KM

3) 6% METALS WET DEPOSITED WITHIN 50 KM OF SOURCE

STATISTICAL APPROACH TO LONG-RANGE TRANSPORT MODELING

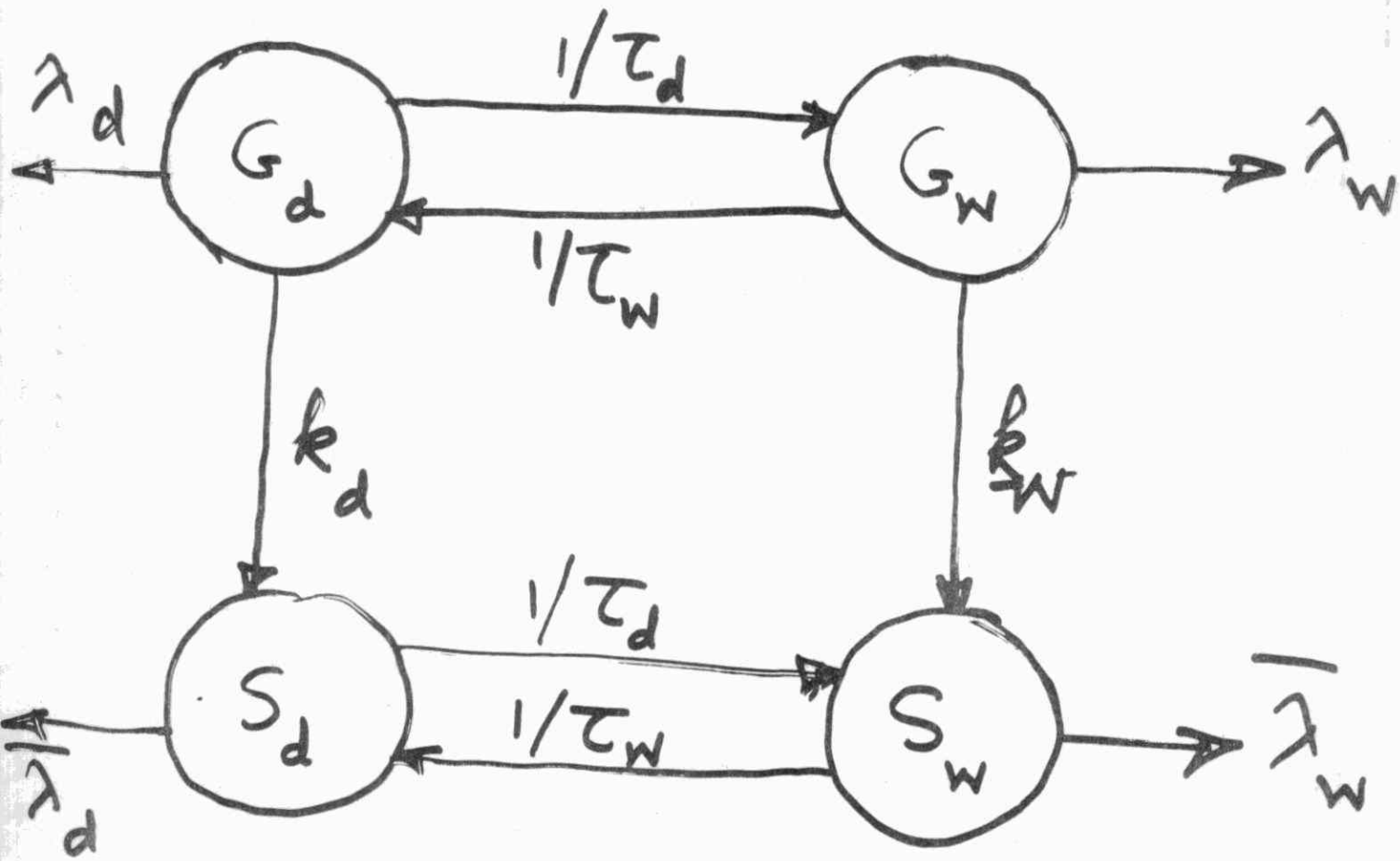
USED PRIMARILY TO ESTIMATE LONG-TERM EFFECTS OF SO_2 (NO_x) EMISSION

PRINCIPAL COMPONENTS ARE:

1) SCAVENGING MODEL – WET AND DRY DEPOSITION

2) DISPERSION MODEL - LARGE SCALE MOVEMENT OF LARGE SCALE WEATHER SYSTEMS

SCAVENGING MODEL



$G = SO_2 \qquad S = SO_4$

$$\lambda_d = \frac{v_d}{h} \quad ; \quad \lambda_w = \frac{v_d}{h} + p$$

$$G_d(0) = (1-f)_p Q_{SO_2} \quad ; \quad G_w(0) = f_p Q_{SO_2}$$

SYSTEM RESULTS IN COUPLED FIRST ORDER DIFFERENTIAL EQUATIONS

LINEAR SYSTEM IS NECESSARY FOR TRAJECTORY MODELS

SOLUTION LOOKS LIKE

$$G = \sum A_i \exp(\alpha_i t)$$

$$S = \sum A_{is} \exp(\alpha_i t) + \sum B_{is} \exp(\beta_i t)$$

INPUTS TO MODEL:

λ_d, $\bar{\lambda}_d$, λ_w, $\bar{\lambda}_w$

τ_d, τ_w

DISPERSION MODEL

$$C(\underset{\sim}{r}) = \frac{1}{f} \int_0^\infty Q(\tau)\, p(\underset{\sim}{r}, \tau, \underset{\sim}{r}_s)\, d\tau$$

$Q(\tau)$ = AMOUNT OF MATERIAL LEFT AT TIME OF TRAVEL τ

$p(\underset{\sim}{r}, \tau, \underset{\sim}{r}_s)$ = PROBABILITY THAT PARTICLE RELEASED AT $\underset{\sim}{r}_s$ WILL BE FOUND AT $\underset{\sim}{r}$ AFTER TIME τ

INPUTS TO MODEL

$Q(\tau)$ = DERIVED FROM SCAVENGING MODEL

$p(\underset{\sim}{r}, \tau, \underset{\sim}{r}_s)$ = DERIVED FROM TRAJECTORY STATISTICS

$$p(\underset{\sim}{r}, \tau, \underset{\sim}{r}_s) = \frac{1}{2\pi h \sigma_x \sigma_y} \exp\left[-\frac{(x - \bar{x}(\tau))^2}{2\sigma_x^2} - \frac{(y - \bar{y}(\tau))^2}{2\sigma_y^2} \right]$$

h = MIXED LAYER HEIGHT

σ_x, σ_y = PARTICLE STANDARD DEVIATIONS ABOUT $\bar{x}, \bar{y}$

INPUTS TO OUR MODEL

$v_d = 1\ cms^{-1}$ (SO_2)

$\overline{v_d} = 0.1\ cms^{-1}$ (SO_4)

$p = 10^{-5} s^{-1}$ (SO_2)

$\overline{p} = 10^{-9} s^{-1}$ (SO_4)

$h = 1500\ m$

$u = 10\ ms^{-1}$

$\sigma_x = u_m t$; $u_m = 10\ ms^{-1}$

$\sigma_y = v_m t$; $v_m = 6\ ms^{-1}$

$\tau_d = 48\ hr$, $\tau_w = 12\ hr$

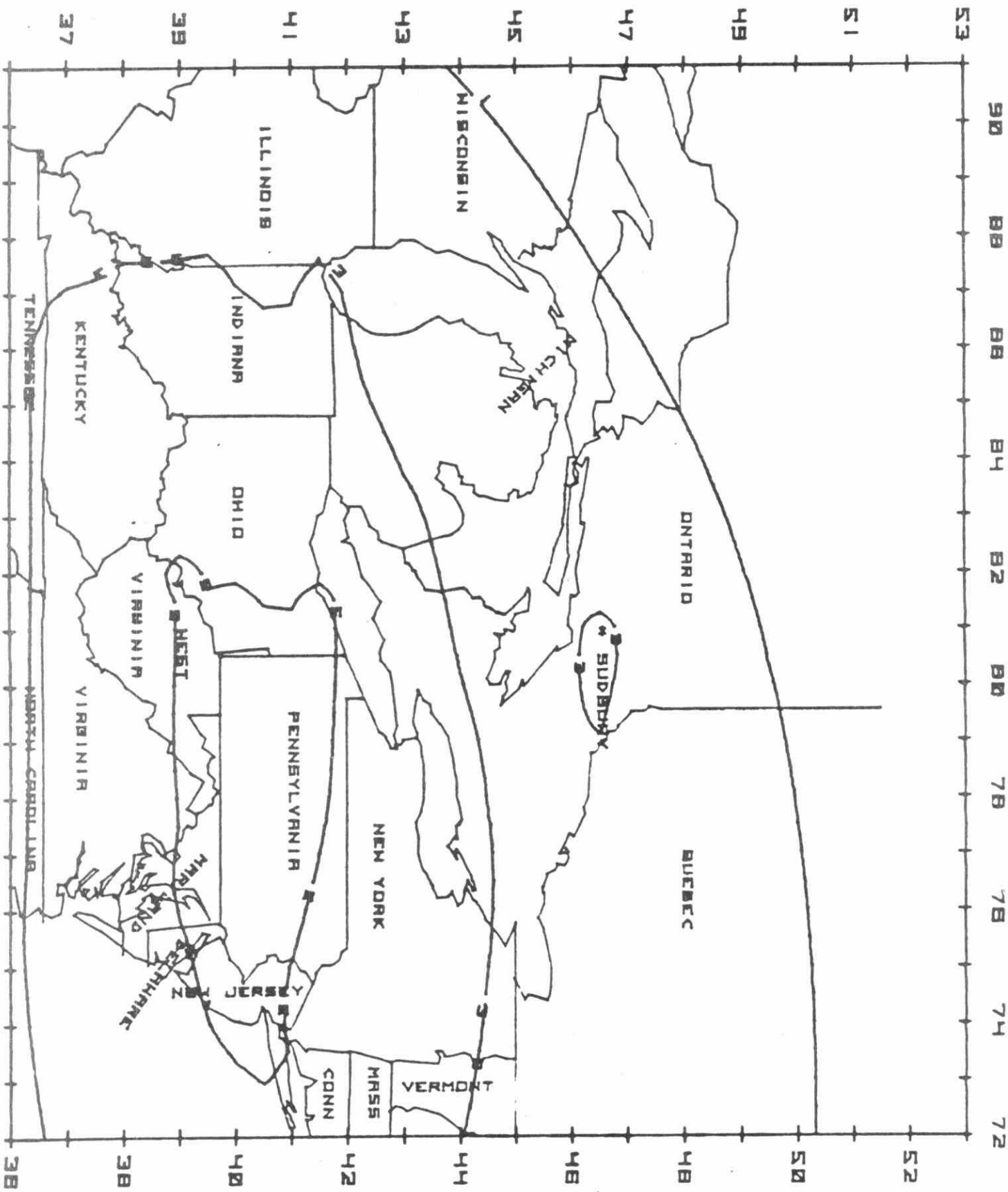
$k_d = 2\%\ hr^{-1}$, $k_w = 5\%\ hr^{-1}$

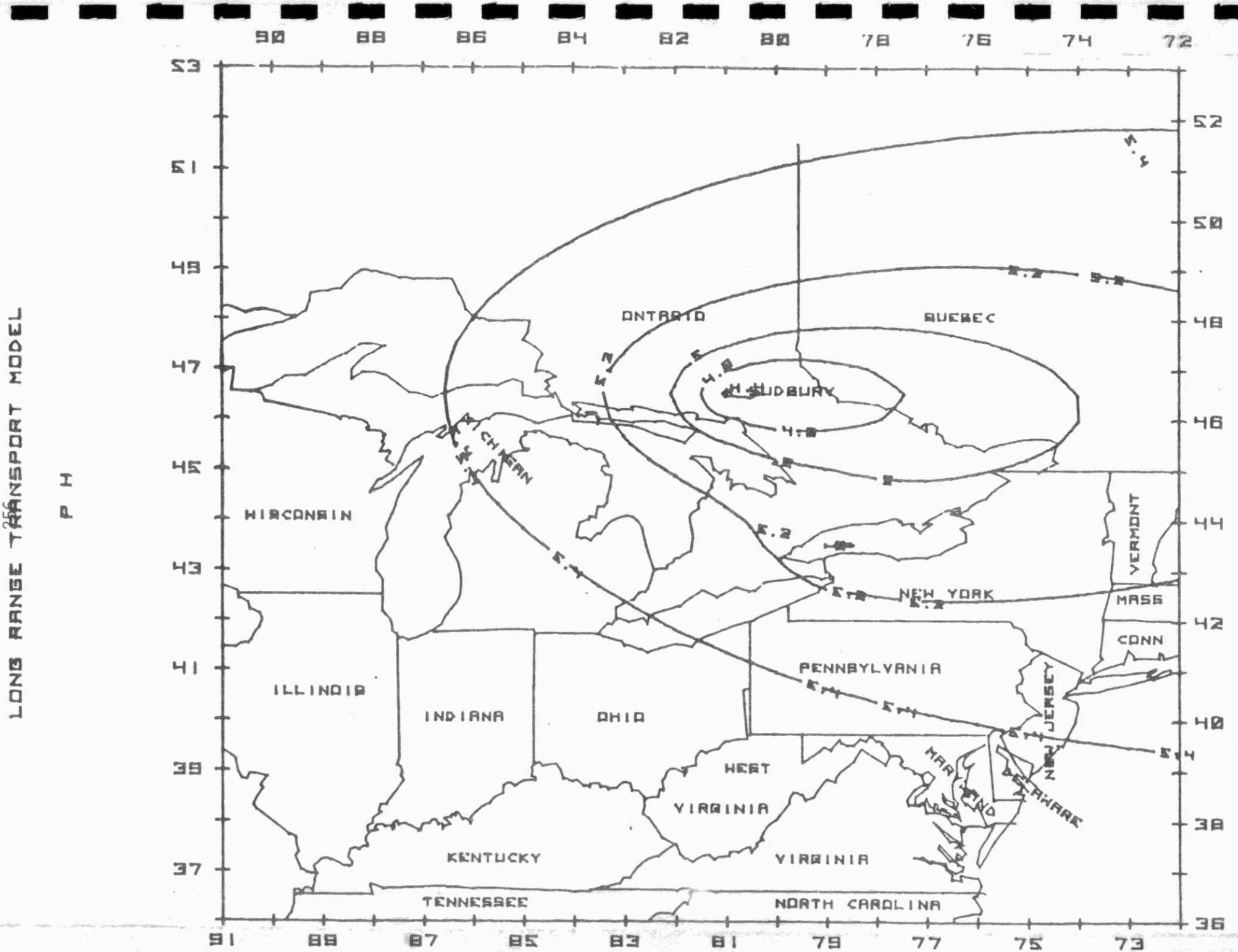
$f_d = 90\%$, $f_w = 10\%$

$Q_{SO_4} / Q_{SO_2} = 0.02$

LONG RANGE TRANSPORT MODEL

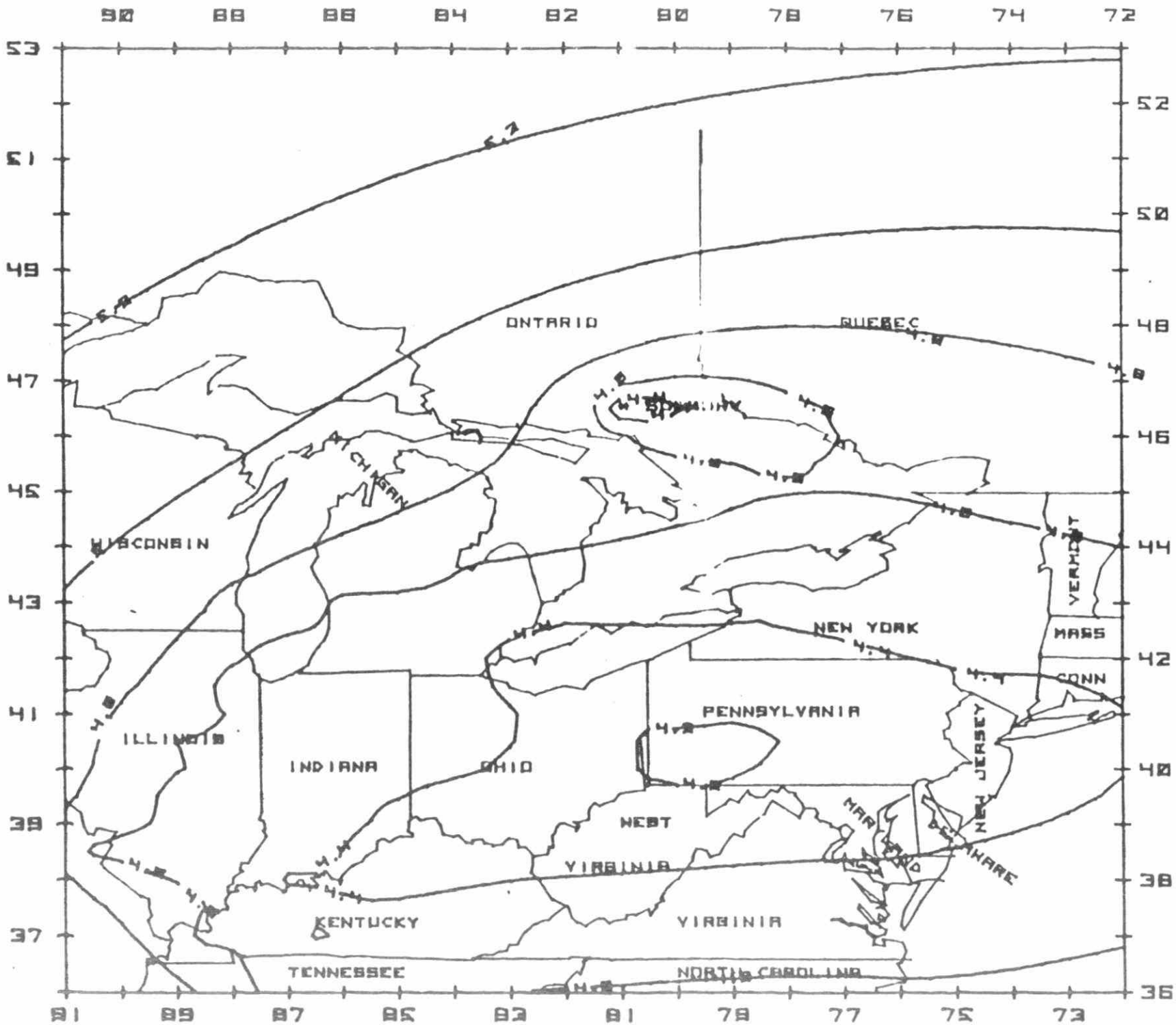
SO_4 AVER CONCENTRATION (UG/M^3)




LONG RANGE TRANSPORT MODEL
P H
256
90 88 86 84 82 80 78 76 74 72
53 51 49 47 45 43 41 39 37
52 50 48 46 44 42 40 38 36
91 89 87 85 83 81 79 77 75 73
ONTARIO
QUEBEC
SUDBURY
MICHIGAN
WISCONSIN
NEW YORK
VERMONT
MASS
CONN
PENNSYLVANIA
NEW JERSEY
ILLINOIS
INDIANA
OHIO
WEST VIRGINIA
MARYLAND
DELAWARE
KENTUCKY
VIRGINIA
TENNESSEE
NORTH CAROLINA

LONG RANGE TRANSPORT MODEL

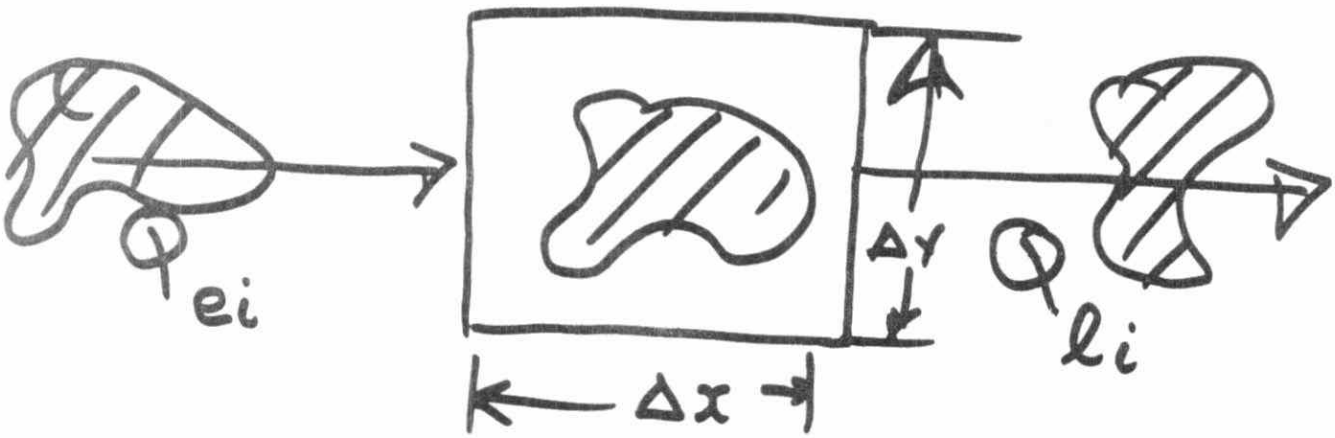
P H



LONG RANGE TRANSPORT MODEL
SO_4 WET CONCENTRATION (UG/M^3)
NORTH CAROLINA
TENNESSEE
VIRGINIA
KENTUCKY
VIRGINIA
WEST
OHIO
INDIANA
ILLINOIS
PENNSYLVANIA
NEW JERSEY
MARYLAND
DELAWARE
CONN
MASS
NEW YORK
VERMONT
MICHIGAN
WISCONSIN
QUEBEC
ONTARIO

SHORT-TERM (MONTHLY) CONCENTRATIONS

PUFF MODEL



$$C = \sum \frac{Q_{ei} + Q_{li}}{2} \frac{\Delta t_i}{T}$$

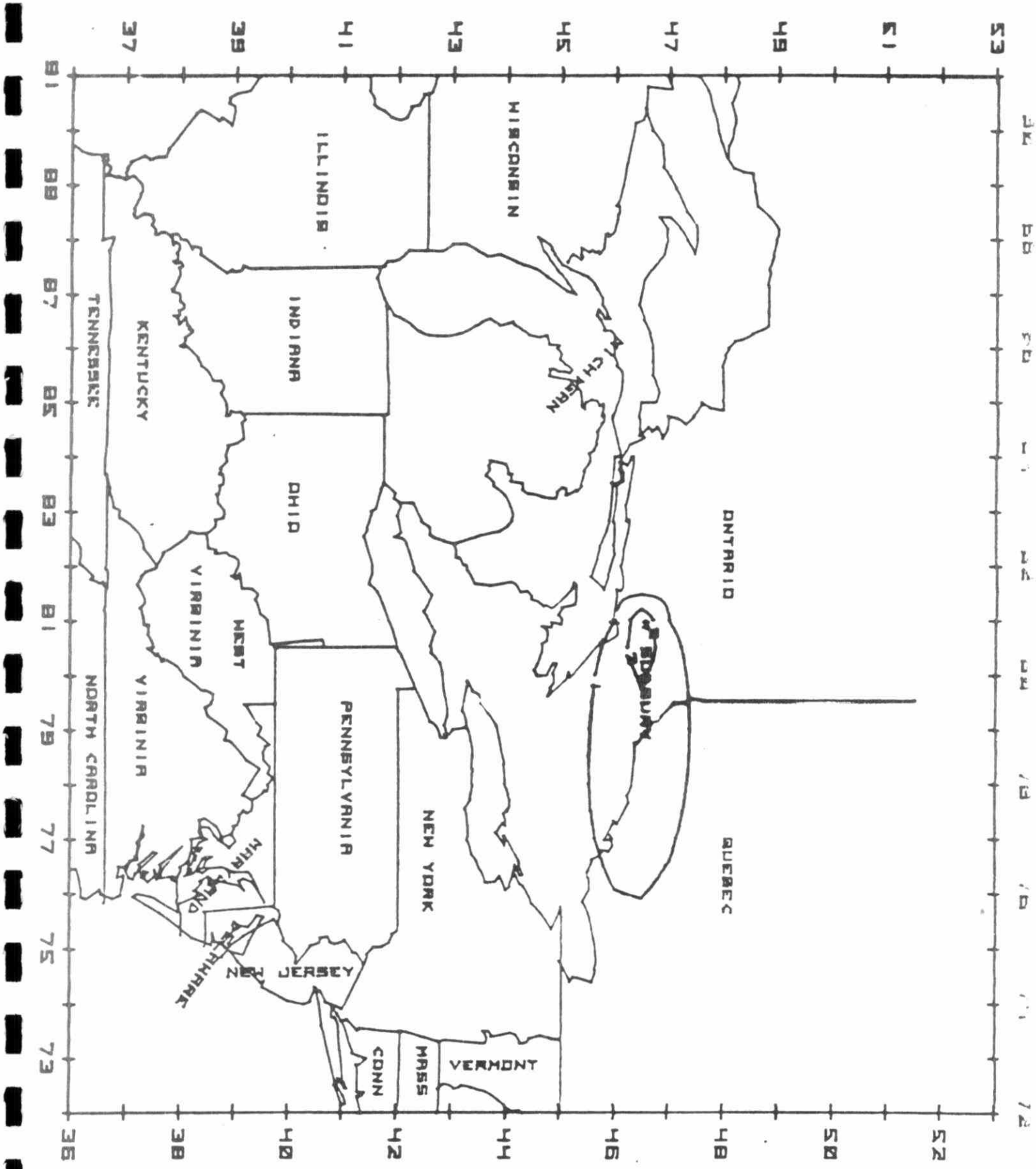
$$Q_{li} = Q_{ei} \times \text{SCAVENGING}$$

LONG RANGE TRANSPORT MODEL

SO_2 AVER CONCENTRATION < $UG/M.^3$ >

LONG RANGE TRANSPORT MODEL

SO_4 AVER CONCENTRATION (UG/M^3)

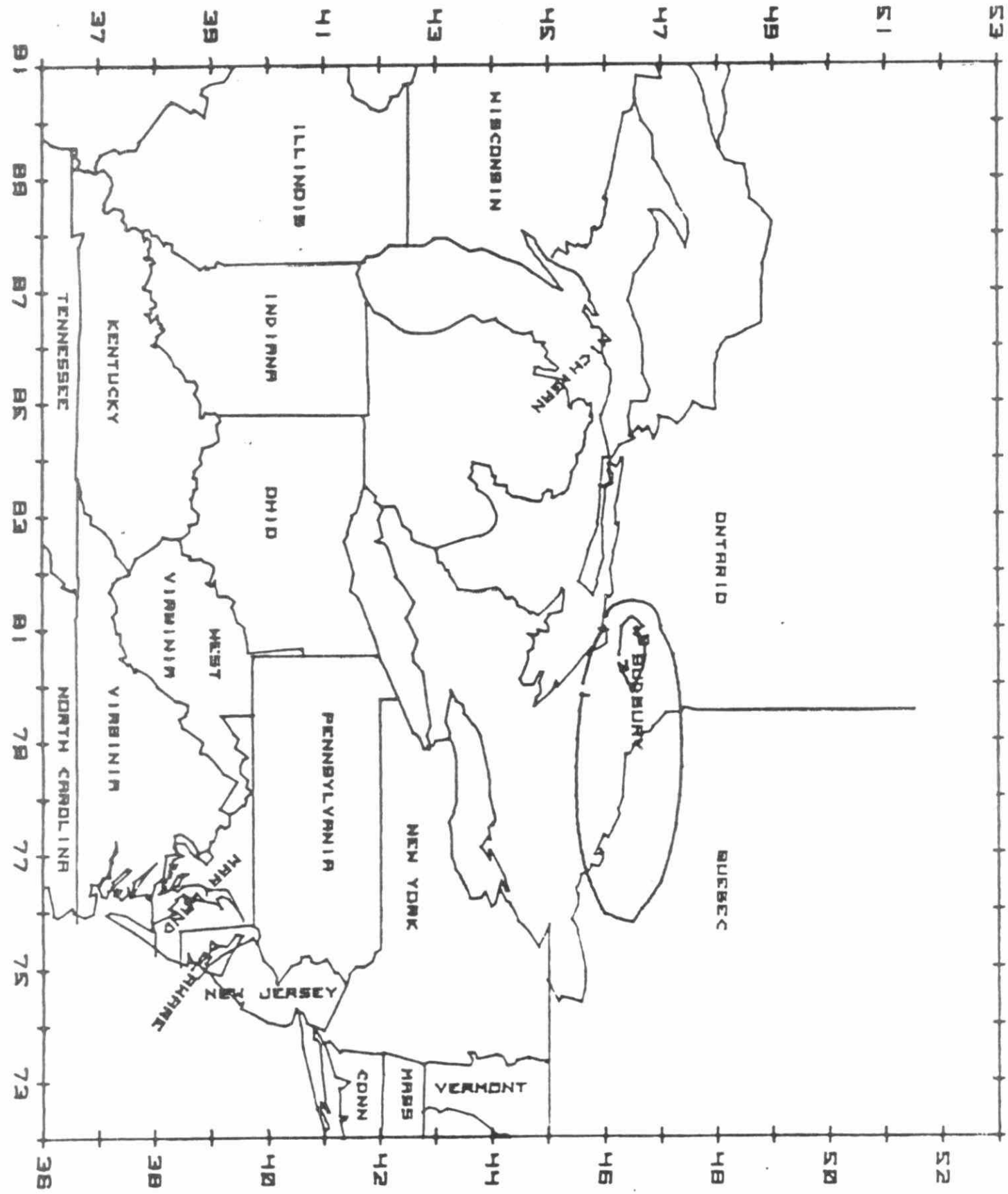


LONG RANGE TRANSPORT MODEL

SO_4 WET CONCENTRATION (UG/M^3)

LONG RANGE TRANSPORT MODEL

SO_4 DRY CONCENTRATION (UG/M^3)



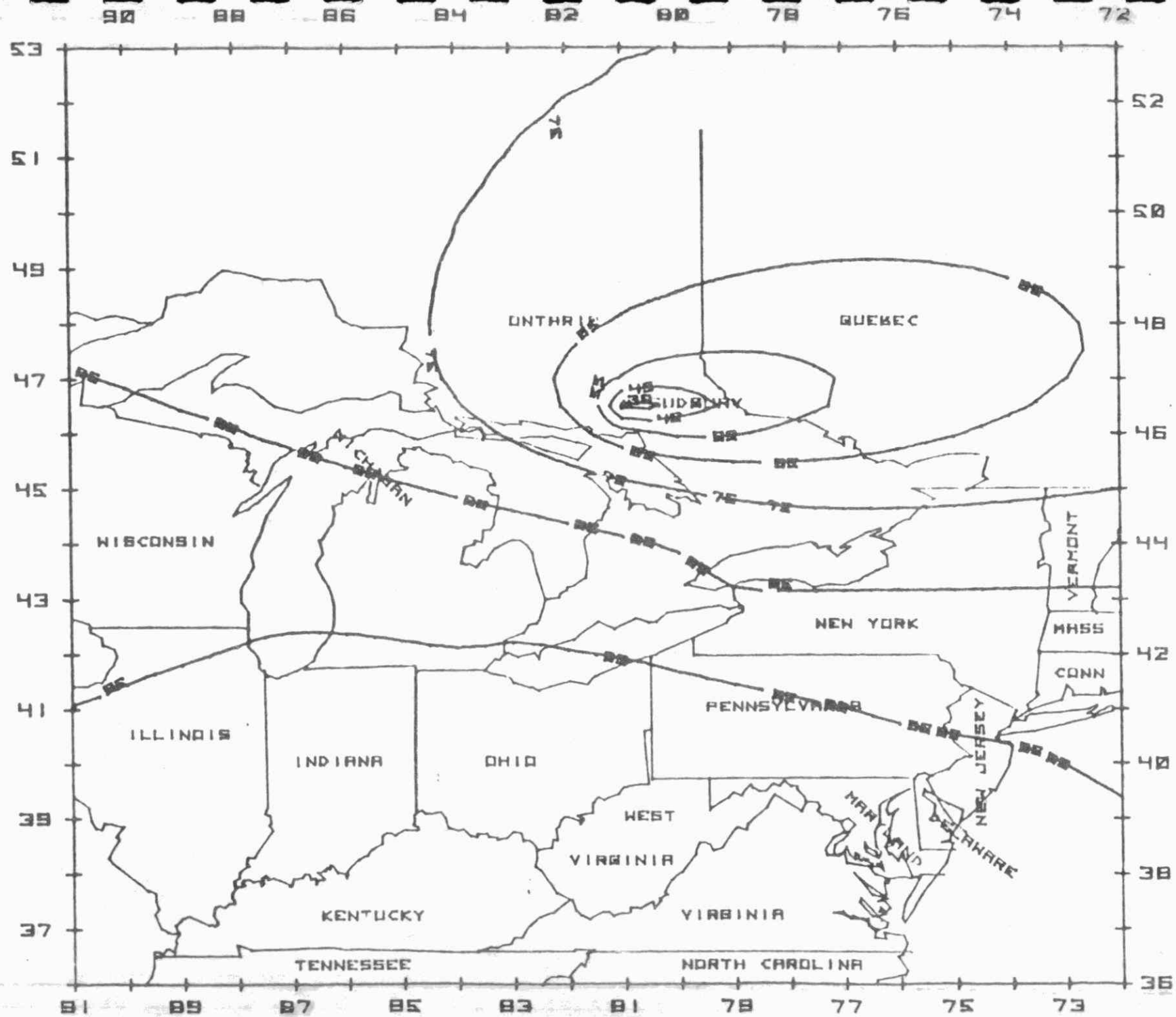
LONG RANGE TRANSPORT MODEL
SO_4 WET CONCENTRATION (UG/M^3)
90 88 86 84 82 80 78 76 74 72
53 51 48 47 45 43 41 39 37
52 50 48 46 44 42 40 38 36
91 89 87 85 83 81 79 77 75 73
ONTARIO
QUEBEC
SUDBURY
MICHIGAN
WISCONSIN
VERMONT
NEW YORK
MASS
CONN
ILLINOIS
INDIANA
OHIO
PENNSYLVANIA
NEW JERSEY
WEST VIRGINIA
VIRGINIA
KENTUCKY
TENNESSEE
NORTH CAROLINA

LONG RANGE TRANSPORT MODEL

SO_4 DRY CONCENTRATION < UG/M^3 >

LONG RANGE TRANSPORT MODEL

SO_4 DRY CONCENTRATION (UG/M^3)



LONG RANGE TRANSPORT MODEL

SO_2 AVER CONCENTRATION < $\mu G/M^3$ >

APPENDIX SIX

"COMPARISON BETWEEN MEASURED AND COMPUTED CONCENTRATIONS OF SULFUR COMPOUNDS IN EASTERN NORTH AMERICA"

E.C. Voldner, M.P. Olson, K. Oikawa and M. Loiselle

Atmospheric Environment Service
4905 Dufferin Street
Downsview, Ontario, Canada
M3H 5T4

A concentration/deposition model has been developed for application to the Long-Range Transport of Air Pollutants (LRTAP) program within the Department of the Environment in Canada. The Lagrangian model computes concentration and deposition fields of sulfur compounds as well as precipitation pH over North America.

Four-day, backward trajectories are computed from three-dimensional objectively analysed windfields, which are available four times a day. The pollutants (SO_2 SO_4) are assumed well mixed throughout the mixing layer. The mixing height varies diurnally and seasonally according to mixing height climatologies. Precipitation data are obtained from twenty-four hour objective analyses and SO_2 source emissions from a North American emission's inventory. Wet and dry deposition and chemical transformation processes are parameterized

Results obtained from the model have been compared with measurements from different monitoring networks in East North America. The networks record quantities such as air concentrations of SO_2 and sulfate and, also sulfate and pH in precipitation at different time resolutions.

The agreement between measured and computed quantities are generally good. The occurrences of air pollution episodes are duplicated in space and time. Average computed and measured concentration/deposition fields are generally within sixty percent and pH values within a few percent of each other.

The paper gives a brief description of the model, shows its sensitivity to changes in values of key parameters and gives results from a comparison study in 1977. Further, some problems encountered when using actual measured data for model comparison will be discussed.

COMPARISON BETWEEN MEASURED AND COMPUTED CONCENTRATIONS OF SULFUR COMPOUNDS IN EASTERN NORTH AMERICA

- MODEL
- PROBLEMS WITH MODEL VALIDATION
- PRELIMINARY COMPARISON BETWEEN MEASURED AND COMPUTED VALUES
- IMPROVEMENTS

2

LAGRANGIAN C/D MODEL

WIND FIELD

- OBJECTIVELY ANALYZED ON CMC GRID (GRIDLENGTH 381 km) AT 1000, 850, 700 AND 500 mb EVERY 6 HOURS.

ASSUMPTIONS

- POLLUTANTS WELL MIXED IN THE VERTICAL TO MIXING HEIGHT.
- $SO_2 \rightarrow SO_4^{2-}$ FIRST ORDER REACTION
- DRY REMOVAL DRY DEPOSITION VELOCITY
- WET REMOVAL WASHOUT RATIO

INPUT

- PRECIPITATION AMOUNTS ARE 24 HOUR TOTALS, OBJECTIVELY ANALYZED AT CMC

- INVENTORIES

  US DATA 1969 - 1970

  CANADIAN DATA 1974 (1978)

DATA

• USA	EPRI SURE	SO_2, $SO_4^=$	IN AIR
	MAP3S	$SO_4^=$,	pH IN PRECIP.
• CANADA	AES	SO_2, $SO_4^=$	AIR
	ONT. HYDRO	$SO_4^=$	IN AIR
	CANSAP	$SO_4^=$,	pH IN PRECIP.

GENERAL PROBLEMS WITH MODEL VALIDATION

- LACK OF UNIFORMITY IN MEASUREMENTS

  CANADA → WET DEPOSITION
  USA → AIR CONCENTRATIONS

- DIFFERENCE BETWEEN NETWORKS (INSTRUMENTS, OPERATING INTERVALS, RESOLUTION)

  GAPS IN DATA

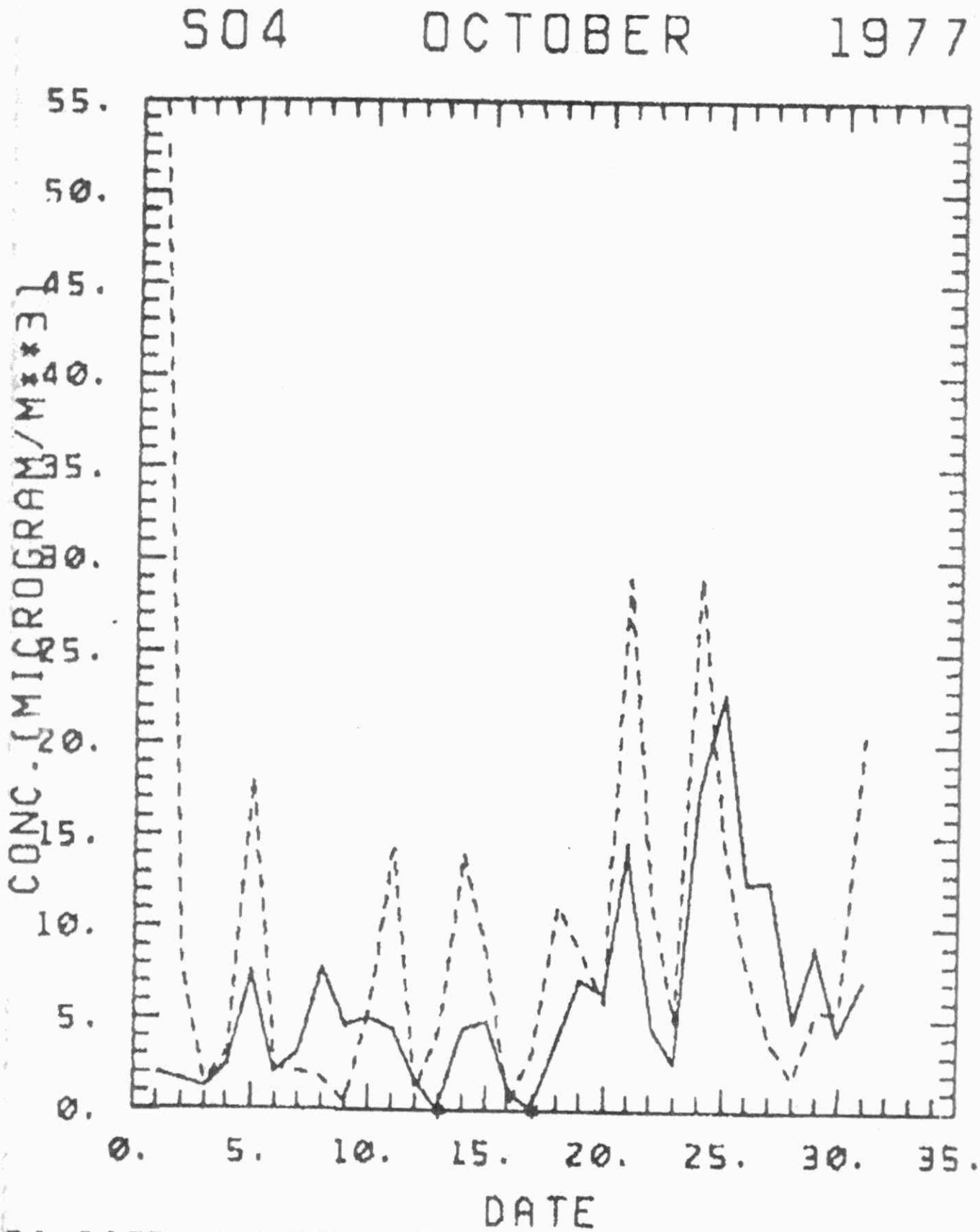
- REPRESENTATIVENESS OF DATA

  - ERROR IN MEASUREMENTS
  - REFLECTION OF LOCAL RATHER THAN REGIONAL EFFECTS
  - GROUND BASED MONITORS

STUDY PERIOD OCT 1977

VALUES OF MODEL PARAMETERS.

TRAJECTORIES	ISOBARIC, 3 DAY
MIXING HEIGHT	CLIMATOLOGICAL
$V_d SO_2$	0.6 cm/s
$V_d SO_4$	0.5 cm/s
αSO_2	10^5
αSO_4	10^6
k	1 %/hr
PRECIP	24 hr AVERAGES

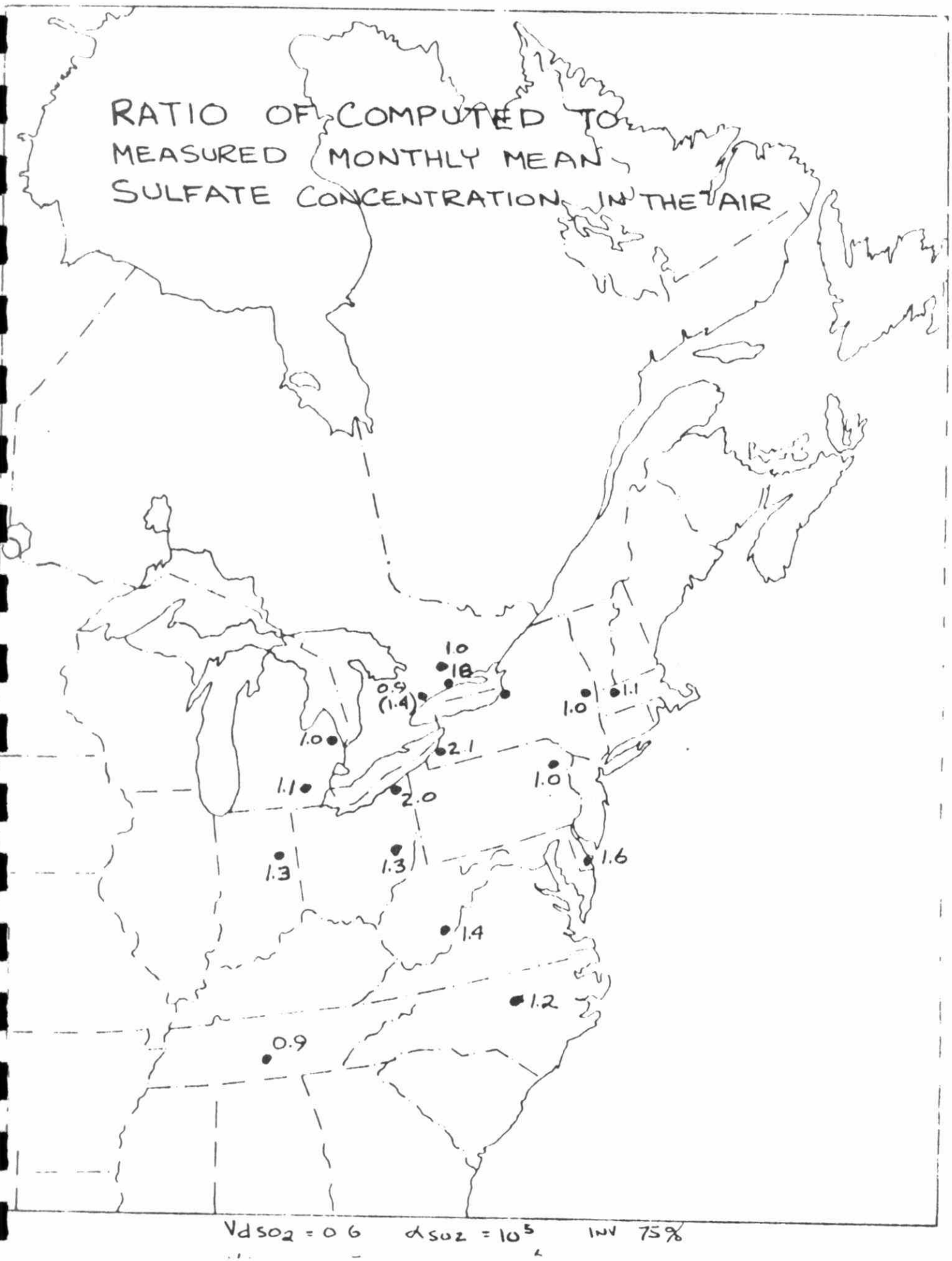


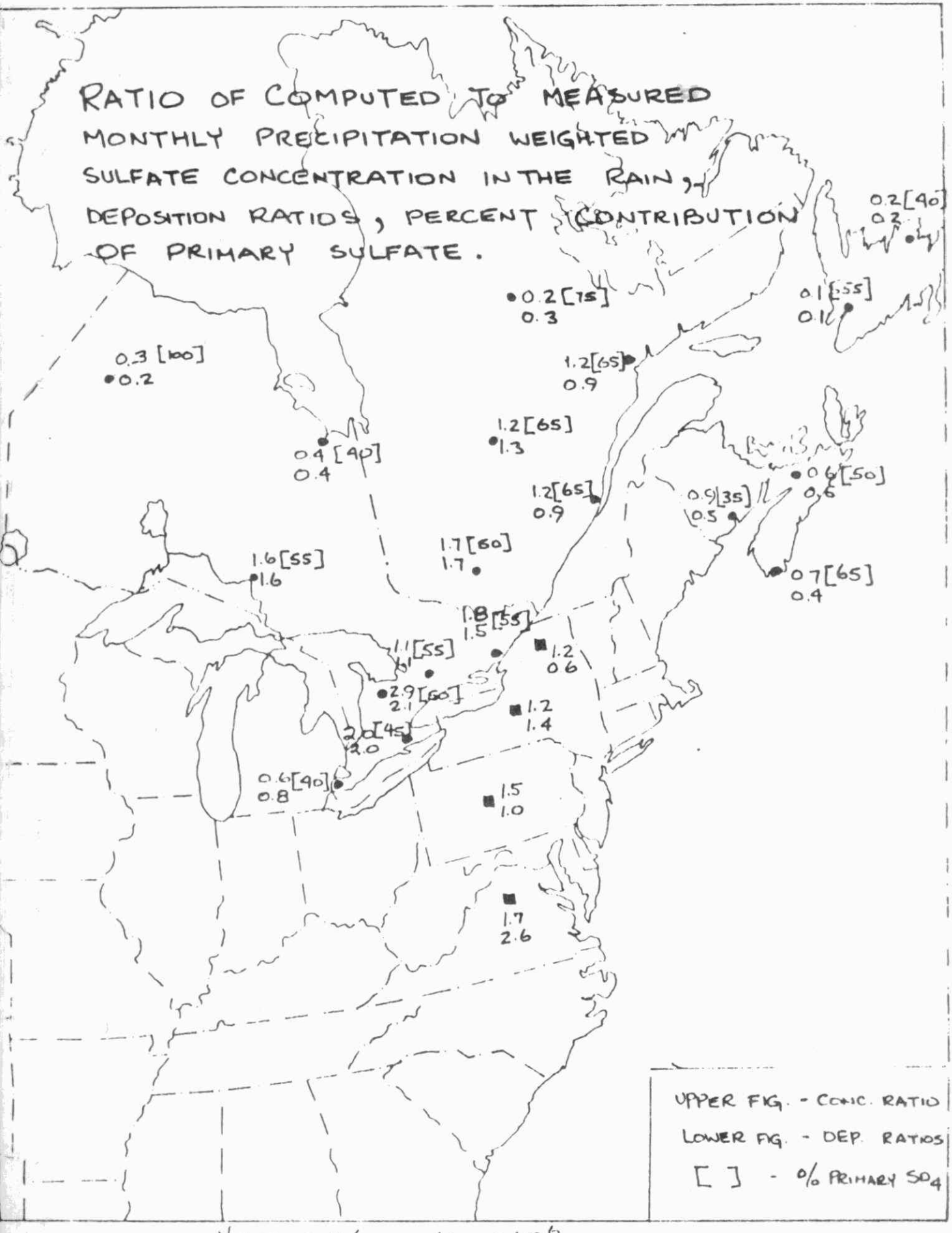
EPRI SITE NUMBER -25

PORT HURON, MI

24 HOUR MEAN

DASHED LINE = COMPUTED CONC.
SOLID LINE = MEASURED CONC.


RATIO OF COMPUTED TO
MEASURED MONTHLY MEAN
SULFATE CONCENTRATION IN THE AIR
1.0
1.8
0.9
(1.4)
1.0
1.1
1.0
2.1
1.1
2.0
1.0
1.3
1.3
1.6
1.4
1.2
0.9
Vdso2 = 0.6
αso2 = 10^5
INV 75%



$V_d SO_2 = 0.6$ $\quad V_d SO_4 = 10^6$

IMPROVEMENTS CURRENTLY UNDER INVESTIGATION

- INTRODUCING A VARIABLE WASHOUT RATIO FOR SO_2 SCAVANGING
- UPDATING THE EMISSIONS INVENTORY IN CO-OPERATION WITH EPRI - SURE AND EPS.
- FINE TUNING THE INPUT PARAMETERS USING SIMULTANEOUS $SO_2 / SO_4^=$ AIR DATA AND EVENT PRECIPITATION DATA BEING GATHERED AT 5 APN NETWORK SITES IN EASTERN CANADA.

APPENDIX SEVEN

THE PREDICTION OF RAIN ACIDITY AND SO_2 SCAVENGING IN EASTERN NORTH AMERICA

L.A. BARRIE

Atmospheric Environment Service

September 1979.

ABSTRACT

The eastern half of the North American continent experiences acidic rain. An approach to predicting that acidity from SO_2 emission rates and meteorological data is suggested. It is based on modelling the atmospheric sulphur cycle and on the strong correlation between hydrogen and sulphate ions in rain collected by the CANSAP and MAP3S precipitation networks. The molar ratio $[H^+]/[SO_4^=]$ in rain is commonly 1.6 - 2 in the northeastern U.S.A. and ~1 in acid sensitive areas of eastern Canada. Using the solution chemistry of sulphur dioxide, it is concluded that dissolved SO_2 can contribute substantially to the acidification of a receptor by rain especially at low temperatures in areas having particulate matter with a low hydrogen ion content. An expression is derived relating SO_2 washout ratio to two parameters, rain water pH and temperature. Ways of incorporating SO_2 washout into sulphur cycle models are discussed.

1. INTRODUCTION

In the last decade serious effects of acidic precipitation associated with anthropogenic emissions of sulphur and nitrogen oxides have been observed in the biosphere (Ambio, 1976; NATO, 1978). Consequently, efforts have been initiated in many countries to develop models that predict the temporal and spatial distribution of the hydrogen ion content of precipitation from known or projected pollutant emission rates and meteorological data (Voldner et al, 1979; Shannon, 1979).

A predictive capability is required in order to assess the impact of long term energy strategies. For instance, it is necessary to anticipate the increase in precipitation acidity in eastern North America if power plants there were to switch to burning coal of a higher sulphur content. In theory, the hydrogen ion content of rain can be predicted by accurately modelling the cycles of all acidic and basic compounds scavenged by rain and then solving the ion balance equation for hydrogen ion concentration. However, in practice this is infeasible. This is, in part, because the cycles of important basic constituents such as ammonia and calcareous windblown dust are poorly understood. In the following discussion, an alternative empirical approach to predicting the hydrogen ion content of rain is suggested for eastern North America. It involves modelling the atmospheric sulphur cycle to predict the sulphate content of rain and then using an empirical relationship between the hydrogen and sulphate ion content of rain revealed by recent data from the Canadian CANSAP and American MAP3S precipitation networks to produce an estimate of rain pH.

Most of the sulphur entering the atmosphere from anthropogenic sources is in the form of sulphur dioxide gas, SO_2. Typically, 95-99% of the total sulphur in the effluent of oil or coal-fired thermal generating stations is in the form SO_2 (Forrest and Newman, 1977). The remainder consists of 'primary' particulate sulphate, mainly sulphuric acid. While being transported through the atmospheric boundary layer (ca. 0-2 km), SO_2 is chemically transformed to 'secondary' particulate sulphate, absorbed at the earth's surface and scavenged by precipitation. It has been observed that dissolved SO_2 can contribute up to 30% (on a molar basis) to the total sulphur content of rain in the northeastern United States (Hales and Dana, 1978) and 14% on the average in rural England (Davies 1979).

In this paper, the role of sulphur dioxide as a rainwater acidifying agent is examined. A quantitative relationship between the SO_2 content of rain, rainwater pH and temperature is derived which can be used in long range transport models to mathematically simulate the SO_2 scavenging process. Methods of calculating precipitation acidity and hence SO_2 washout are demonstrated for various rainwater chemistry data sets.

2. THEORY OF SO_2 - WASHOUT

In models, the sulphur dioxide concentration in rain is often calculated from predicted, atmospheric concentrations of the gas using a dimensionless washout ratio W_{SO_2} (Slinn et al, 1978) defined as

$$W_{SO_2} = \frac{[SO_2]_r}{[SO_2]_a} \qquad (1)$$

Subscripts 'r' and 'a' denote rain and air, respectively. The wet removal rate F (dimension $ML^{-2}T^{-1}$) is then given by

$$F = W_{SO_2} \; I \; (SO_2)_a \qquad (2)$$

I is precipitation intensity (dimension LT^{-1}). It has been common practice to use a constant 'representative' washout ratio to calculate the rate of removal of SO_2 by precipitation, (e.g. Henmi and Reiter, 1978). As will be shown below, W_{SO_2} is not constant but rather strongly dependent on rain pH and temperature. The relationship is governed by the equilibrium solution chemistry of sulphur dioxide which is described by the following equations.

$$K_H = \frac{[SO_2 \cdot H_2O]_r}{[SO_2]_a} \qquad (3a)$$

$$K_1 = \frac{[H^+]_r \; [HSO_3^-]_r}{[SO_2 \cdot H_2O]_r} \qquad (3b)$$

$$K_2 = \frac{[H^+]_r \; [SO_3^=]_r}{[HSO_3^-]_r} \qquad (3c)$$

K_H, K_1 and K_2 are equilibrium constants. Square brackets represent molar concentrations. Sulphur dioxide exists in solution as: physically-dissolved SO_2 ($SO_2 \cdot H_2O$), bisulphite ion (HSO_3^-), and sulphite ion ($SO_3^=$). Barrie (1978) has shown that for the range of precipitation pH's commonly observed in the atmosphere (3-6) over 95% of total-dissolved SO_2 is in the form of bisulphite ion (i.e. $[SO_2]_r \equiv [HSO_3^-]_r$). Thus, under equilibrium conditions equations 1, 3a and 3b yield:

$$W_{SO_2} = \frac{[HSO_3^-]_r}{[SO_2]_a} = \frac{K_1 K_H}{[H^+]_r} \qquad (4a)$$

or, in terms of pH

$$\log_{10} W_{SO_2} = \log_{10}(K_1 K_H) + pH \qquad (4b)$$

In deriving equation 4, the assumption was made that SO_2 in the air is in equilibrium with SO_2 in the rain. Hales (1978) introduced an objective criteria which must be satisfied in order for 'equilibrium scavenging' to occur. He points out that beyond 20 stack heights of a point source the criteria is usually satisfied. Thus for the purposes of regional and global transport modelling, equation 4 for W_{SO_2} is valid. One must, however, be careful to avoid using it in situations in which the Hales-criteria is not met. (Non-equilibrium scavenging is more complex requiring, among other things, a knowledge of the raindrop spectra, Barrie 1978).

The equilibrium constants K_1 and K_H are temperature dependent (Table 1) and their product K_1K_H determines the temperature dependence of the SO_2 washout ratio. Over the range 273.1 - 303.1 ^oK (0-30C), K_1K_H is related to temperature T (^oK) by the following empirical equation:

$$K_1K_H = 6.22 \times 10^{-8} \exp(4755.5/T) \qquad (5)$$

A graphical illustration of the dependence of W_{SO_2} on pH and temperature is given in Figure 1. W_{SO_2} values that are likely to occur in the atmosphere are denoted by the hatched area. They fall within a range 10^3 - 10^6. The strong dependence on pH and temperature illustrated in Figure 1 emphasizes the need to account for it in long range transport models rather than neglecting it as is often done by using a constant 'representative' W_{SO_2} value (W_{SO_2} increases 10 fold for unit increase in pH and 4.3 fold for a change in temperature from 25 to 0C).

Another type of SO_2-washout parameterization is sometimes used in models. A scavenging coefficient λ has been utilized to

calculate the SO_2-removal rate R due to precipitation scavenging in simple box or layer models (McMahon et al, 1976). R is assumed to be directly proportional to the ambient SO_2 concentration where λ is the proportionality constant. If washout is the only sink for SO_2

$$\lambda = -\left(\frac{d \ln [SO_2]_a}{dt}\right)_{\text{during rain event}} \qquad (6)$$

Values of λ can be extracted from time series measurements of ambient SO_2 concentrations during precipitation events (Maul, 1978). They are related to the washout ratio by the following equation

$$\lambda = \frac{W_{SO_2} I}{H} \qquad (7)$$

where H is the depth of the box in a one layer model or of a layer in a multilayer model and I is precipitation intensity.

3. THE CONTRIBUTION OF DISSOLVED SO_2 TO THE ACIDITY OF RAIN

The fraction of the total hydrogen ions in wet deposition that are contributed by dissolved SO_2, f, is an indicator of the role that precipitation scavenging of SO_2 plays in the acidification of a receptor. In most natural receptors including oceans, lakes and calcareous soil, dissolved SO_2 is eventually oxidized to sulphate. Hence two hydrogen ions are released for each SO_2 molecule entering a receptor in rain. Assuming that there are B hydrogen ions associated with each sulphate ion present in rain reaching the ground, f is given by:

$$f = \frac{2[HSO_3^-]_r}{B[SO_4^=]_r + 2[HSO_3^-]_r} \qquad (8)$$

In the ideal situation where only sulphate aerosols and SO_2 are present in the system, B would be 2, 1, or 0 if the aerosol scavenged

consisted of sulphuric acid (H_2SO_4), ammonium bisulphate (NH_4HSO_4) or ammonium sulphate ($(NH_4)_2SO_4$), respectively. Later in this paper evidence will be presented to show that in most of eastern North America there is a strong correlation between hydrogen and sulphate ions. Consequently, the formulation for f in equation 8 is far more versatile than it appears to be at first glance.

f can be related to parameters commonly predicted in long range transport models by defining a washout ratio for sulphate W_{SO_4}, similar to that for SO_2 in equation 1. Using equations 3a, 3b, 4a and the following expression for the hydrogen ion concentration in collected rain:

$$[H^+]_r = B[SO_4^=]_r + [HSO_3^-]_r \qquad (9)$$

one obtains an equation for f in terms of commonly measured variables.

$$f = \frac{2\,W_{SO_2}\,[SO_2]_a}{2W_{SO_2}[SO_2]_a + B\,W_{SO_4}[SO_4^=]_a} \qquad (10)$$

where $$W_{SO_2} = \frac{K_1 K_H}{\frac{B}{2}[SO_4^=]_a\,W_{SO_4} + \sqrt{\left(\frac{B}{2}(SO_4^=)_a\,W_{SO_4}\right)^2 + K_1\,K_H\,(SO_2)_a}} \qquad (11)$$

The dependence of f on $[SO_2]_a$, $[SO_4]_a$ and temperature is shown in Figures 2 and 3 for B values of 2 and 1, respectively. A sulphate washout ratio of 5×10^5 was chosen as typical for eastern Canada by examining data obtained in the Canadian Intensive Sulphate Study of August 1976 (Intensive Sulphate Study 1976). During that study sulphate washout ratios ranged from 3×10^5 to 8×10^5.

In order to demonstrate the importance of dissolved SO_2 as a contributor of hydrogen ions to wet deposition consider the following typical situations:

1. A power plant plume 100 km from the source.

   typically $[SO_2]_a$ = 200 μg m^{-3} (70 ppb)

   $[SO_4^=]_a$ = 10 μg m^{-3}

   B = 2 (sulphuric acid)

   f = 0.20 at 25°C (Fig. 2)

   0.50 at 0°C

2. A polluted maritime tropical air mass in the American Industrial Northeast.

   typically $[SO_2]_a$ = 100 μg m^{-3} (35 ppb)

   $[SO_4^=]_a$ = 10 μg m^{-3}

   B = 2 (MAP3S data) (see Section 4)

   f = 0.11 at 25°C (Fig. 2)

   0.34 at 0°C

3. A polluted maritime-tropical air mass at a rural site in southeastern Canada (e.g. Ottawa region)

   typically $[SO_2]_a$ = 80 μg m^{-3} (28 ppb)

   $[SO_4^=]_a$ = 10 μg m^{-3}

   B = 1 (CANSAP data) (see Section 4)

   f = 0.30 at 25°C (Fig. 3)

   0.57 at 0°C

Dissolved sulphur dioxide can contribute a sizeable fraction of the total hydrogen ions entering a receptor during a rain event (in the above examples, f values ranged from 11 - 30% at 25°C and from 34 - 57% at 0°C). If long range transport models neglected this source of acidity considerable error would be introduced into deposition

estimates especially (i) during weather having near zero temperatures and (ii) in areas having an aerosol with a low hydrogen ion content. Northeastern Canada during the fall fulfills both these conditions. Cold rains scavenge air containing what was originally sulphuric acid aerosol that has been at least partially neutralized by ammonia on its 2 - 6 day journey from the source. SO_2 washout will therefore be important as a source of hydrogen ions.

4. OBSERVED CORRELATIONS BETWEEN HYDROGEN AND SULPHATE IONS IN RAIN

The composition of monthly precipitation samples collected at 25 CANSAP (Canadian Network For Sampling Precipitation) sites in eastern Canada between May and September 1977 and 1978 as well as of event samples collected at four MAP3S (Multistate Atmospheric Power Production Pollution Study) in the U.S. industrial northeast during the same period was examined (site locations Figure 4, site names Tables 2 and 3). A linear regression analysis of $[H^+]_r^{obs}$ and $[SO_4^=]_r^{obs}$ revealed significant correlations between the two parameters at many sites. All four MAP3S sites (Table 3) have very significant correlations (R values for 40-60 samples greater than 0.88). Of the 25 CANSAP sites in eastern Canada (Table 2) the correlation was significant at the 1% level for thirteen. Of the twelve sites having no correlation at the 1% level, five (Trout Lake, Pickle Lake, Atikokan, Moosonee, Fort Chimo) were remote ones having pH's above 5 and six (Windsor, Simcoe, Mt. Forest, Kingston, St. Hubert, Quebec City) had elevated calcium levels. The remaining site, Charlo, showed a correlation bordering on significant but only seven monthly samples were available. A plot of the correlation coefficient R for both U.S. and Canadian sites on a map (Figure 5) reveals a pattern

(R values are underlined if they show a significant correlation at the 1% level) Downwind of major source regions (Figure 6), hydrogen and sulphate ions are strongly related at sites whose local surface geology is non-calcareous. Locations in the limestone-based St. Lawrence lowlands have poor correlations. This is probably due to alkaline calcium particles in the rain that originate either from wind-blown dust scavenged by the rain or from wind-blown dust that entered the sample after collection (despite the use of wet-only samplers). A difference between the chemistry of rain collected at on-shield and off-shield sites in south-central Ontario has been observed previously and attributed to the greater abundance of alkaline soil particles at off-shield sites (Dillon et al, 1977).

The slope B of the linear regression equation

$$[H^+]_r = A + B\,[SO_4^=]_r^{measured} \qquad (12)$$

is plotted in Figure 7 for those sites showing a significant correlation. When the intercept A is not negligible it is also plotted in brackets. At most sites in the Canadian Shield

$$[H^+]_r = B[SO_4^=]_r \qquad (13)$$

B-values are close to 1 in this region. The observed spatial distribution of B-values is most easily interpreted by considering SO_2 emissions (Figure 6). Maximum B-values of 2 are found at Penn State immediately downwind of the major sources of the Pittsburg-Cincinnati area. As the distance between source and sampler increases, B drops attaining a value of 1 in the Canadian Shield Region of Ontario and Quebec. Caution should be exercised in interpreting the MAP3S and CANSAP data sets, for they differ. In the MAP3S network, dissolved-SO_2 and sulphate were measured separately. Thus $[SO_4^=]_r^{obs}$ is the ac-

tual sulphate in the rain. In the CANSAP network, dissolved SO_2 is oxidized to sulphate before analysis so that $[SO_4^{=}]_r^{obs}$ is the sum of $[SO_4^{=}]_r$ and $[HSO_3^{-}]_r$.

It can be shown that if m is the molar fraction of total sulphur in rain that is dissolved SO_2 and if there are B hydrogen ions per sulphate ion in rain reaching the ground, then an empirical relationship of the form shown in equation 13 between $[H^+]_r^{obs}$ and $[SO_4^{=}]_r^{obs}$ yields $D = \left(\frac{B - 2m}{1 - m}\right)_{CANSAP}$ (14)

for CANSAP data (or for any other precipitation data where only total sulphate is available) and:

$$D = \left(B - \frac{m}{1-m}\right)_{MAP3S} \quad (15)$$

for MAP3S data. Bearing in mind that the correlations reported above were for rain falling between May and September m values of 0 for the northeastern U.S. (Hales and Dana, 1979) and 0.1 for the somewhat colder Canadian Shield Region are realistic. Thus for the MAP3S area $D = B \approx 1.6 - 2$ and for the Canadian Shield $D = B - .11 \approx 0.9$.

An important result of the above examination of the relationship between pH and sulphate in rain is that empirical relationship exists in those areas that are most sensitive to acidic precipitation, namely, in the bedrock shield areas of Canada, the Appalachian Mountain Region and the forested areas of eastern Canada. It is in these areas that an accurate prediction of rainwater acidity is especially valuable. In the following section, ways of utilizing observed correlations in models to calculate acidity and SO_2-washout are outlined.

5. INCORPORATING SO_2-WASHOUT INTO MODELS

In section 2, it was shown that dissolved-SO_2 is an important contributor to the acidity of rain and that there is a need to incorporate SO_2-scavenging into models. In this section, ways of calculating SO_2-washout and the pH of precipitation are suggested.

Order of Magnitude Estimates:

One of the cruder estimates of SO_2-washout in achieved by using a 'representative' W_{SO_2}-value and equation 2 to obtain a deposition rate. To choose W_{SO_2} for a particular site one can reduce the number of possible values (Figure 1) by considering the range of pH measured in rain at the site. For example, the pH of summer rain at four MAP3S sites in the eastern U.S. (Table 3) has a range of about 1.0 pH unit (a ten fold range of $[H^+]$). The corresponding uncertainty in a 'representative' washout ratio obtained by inserting the precipitation-weighted mean pH into equation 4 is about a factor of 3. Thus for order of magnitude estimates in the MAP3S region this approach is acceptable. However if more accurate estimates are required this approach is inadequate.

Parameterization For Long Range Transport Models:

The correlation between hydrogen ion and sulphate in rain in eastern North America can be used in long range transport models to predict the acidity and dissolved-sulphur-dioxide content of rain.

Three cases will be considered and for each, expressions given for $[H^+]_r$ and W_{SO_2} in terms of model-predicted parameters.

CASE 1: SO_2 Is The Main Acidifying Agent

Then equation 2 yields

$$[H^+]_r^{pred} = [HSO_3^-]_r = \sqrt{K_1 K_H [SO_2]_a} \qquad (16)$$

and

$$W_{SO_2} = \sqrt{\frac{K_I K_{II}}{[SO_2]_a}} \qquad (17)$$

The relative contribution of SO_2 and sulphate aerosols to precipitation pH was investigated in order to identify those situations in which SO_2 is the main acidifying agent. The dependence of the pH of rain on sulphate aerosol concentrations was calculated for a range of atmospheric SO_2 concentrations (Figures 8 and 9). A sulphate washout ratio of 5×10^5, the same as that used in section 3, was chosen. In addition, it was assumed that to each sulphate ion in rain there correspond 2 (Figure 8) and 1 (Figure 9) hydrogen ions. As shown by observational evidence discussed in the previous sections, this assumption is valid for most acid sensitive areas of eastern North America. Situations in which sulphur dioxide is pH controlling are represented by a point falling on a horizontal segment of the curves in Figures 8 and 9. Those in which sulphate aerosols control pH fall on the sloping dashed line.

Typically, in eastern North America $[SO_4^=]_a$ is 1 - 100 µg m^{-3}, $[SO_2]_a$ is 1 - 1000 µg m^{-3} and $[SO_4^=]_a / [SO_2]_a$ ranges from 0.01 to 1 (increasing away from the source). The acidity of rain is therefore usually controlled by both sulphur dioxide and acidic particulate matter.

CASE 2: $[H^+]_r^{obs}$ and $[SO_4^=]_r^{obs}$ Are Correlated, Sulphate Is That Actually Occurring In Rain Reaching The Ground And Does Not Include That From Oxidation Of Dissolved SO_2 After Sample Collection.

Results from the MAP3S network (Table 3) are particularly suitable for this treatment since sulphates and dissolved-SO_2 are

analyzed separately. If the observed correlation at a site is

$$[H^+]_r^{obs} = A + B[SO_4^=]_r^{obs} \quad (18)$$

then $$[H^+]_r^{pred} = A + B\, W_{SO_4} [SO_4^=]_a^{pred} \quad (19)$$

and from equation 3a

$$W_{SO_2} = \frac{K_1 K_H}{A + BW_{SO_4} [SO_4^=]_a^{pred}} \quad (20)$$

If all predicted input parameters are correct, $[H^+]_r^{obs}$ and $[H^+]_r^{pred}$ are equal and represent the actual pH of rain.

CASE 3: $[H^+]_r^{obs}$ and $[SO_4^=]_r^{obs}$ Are Correlated, Sulphate Consists Of That In Rain Plus That From Oxidation Of Dissolved SO_2 After Sample Collection.

This situation is applicable to data from the Canadian CANSAP Network (Table 2) and Air And Precipitation Monitoring Network (APN) in eastern Canada as well as to that from U.S. NADP Network (Galloway et al, 1978). In these networks dissolved SO_2 is analyzed as sulphate.

In this case, the observed hydrogen ion concentration is related to the actual hydrogen ion concentration in rain by

$$[H^+]_r^{obs} = [H^+]_r^{act} + [HSO_3^-]_r \quad (21)$$

It is also empirically related to observed sulphate.

$$[H^+]_r^{obs} = A + B[SO_4^=]_r^{obs} \quad (22a)$$

$$= A + B\left([SO_4^=]_r^{act} + [HSO_3^-]_r\right) \quad (22b)$$

Eliminating $[H^+]_r^{obs}$ from equations 21 and 22b and using equation 3 to eliminate $[HSO_3^-]_r$ one obtains

$$[H^+]_r^{act} = X + \sqrt{X^2 + (B-1)\, K_1 K_H [SO_2]_a^{pred}} \quad (23)$$

where $X = A + B\, W_{SO_4}\, [SO_4^{=}]_a^{pred}$ (24)

and $[H^+]_r^{pred} = [H^+]_r^{act} + \dfrac{K_1 K_H [SO_2]_a^{pred}}{[H^+]_r^{act}}$ (25)

If all predicted input parameters are correct $[H^+]_r^{obs}$ and $[H^+]_r^{pred}$ are equal and are related to $[H^+]_r^{act}$ by equation 25. The washout ratio is given by

$$W_{SO_2} = \frac{K_1 K_H}{[H^+]_r^{act}} \quad (26)$$

and equation 23.

6. CONCLUSION

Based on the equilibrium solution chemistry of sulphur dioxide, an expression was derived relating the ratio of dissolved SO_2 in rain to SO_2 in air to the temperature and pH of the rain. In addition, the contribution of sulphur dioxide to precipitation acidity was shown to be significant. Consequently, it is important that precipitation scavenging of sulphur dioxide be included in models. In order to do this one must be able to predict precipitation acidity, an exercise which, by itself, yields valuable results. Since one cannot hope to model the cycles of all atmospheric substances that influence precipitation acidity accurately enough to predict rainwater acidity, another approach is needed. Fortunately, as illustrated by data from Canadian and U.S. precipitation networks there is a strong relationship between the hydrogen ion and sulphate ion content of rain in acid sensitive areas of eastern North America. This enables one to predict precipitation acidity from models of the sulphur cycle which is probably understood quantitatively better than that of any other acidifying agent. The correlation between

hydrogen and sulphate ions does not mean that nitric oxides are unimportant in the acidic rain problem. On the contrary, one finds that sulphate, nitrate and hydrogen ions are correlated in rain. However, until the cycles of nitric oxides and ammonia are better understood, the best approach to pH prediction is to model the sulphate cycle, to calculate the sulphate content of rain and then to use observed empirical relationships between sulphate and hydrogen ions to predict pH. The relationships usually take the form

$$[H^+] = B\ [SO_4^=]$$

where B is ~2 in the American industrial northeast and ~1 in southern Canada east of Lake Superior. Sulphur dioxide washout can be calculated using the appropriate equation outlined in section 5.

In closing it should be emphasized that perhaps the greatest uncertainty in the acidity calculation outlined in this paper is the washout ratio for sulphate aerosols. More routine simultaneous observations of storm-type, sulphate aerosol size distribution, rain drop size distribution, and precipitation sulphate concentrations are sorely needed in order to parameterize sulphate aerosol washout.

ACKNOWLEDGEMENTS

The author thanks Mr. R. Berry for his assistance in analyzing the CANSAP precipitation data and Drs. E. Voldner and D.M. Whelpdale for their comments.

References

Ambio, 1976. Vol. 5-6, Proc. Of The Int. Conf. On The Effects Of Acid Precipitation, Telemark, Norway, June 14-19.

Barrie, L.A., 1978. An Improved Model Of Reversible SO_2-Washout by Rain, Atmos. Envir., 12, 407-412.

Davies, T.D., 1979. Dissolved Sulphur Dioxide And Sulphate In Urban And Rural Precipitation, (Norfolk, U.K.), Atmos. Envir. 13, 1275, 1286.

Dillon, P.J., D.S. Jeffries, W. Snyder, R. Reid, N.D. Yan, D. Evans J. Moss, and W.A. Schneider, 1977. Acidic Precipitation In South-Central Ontario: Recent Observations Ontario Min. Envir. Publication, Box 213, Rexdale, Ontario.

Forrest, J. and L. Newman, 1977. Further Studies On The Oxidation of Sulphur Dioxide In Coal-Fired Power Plant Plumes, Atmos. Envir., 11, 465-474.

Galloway, J.N., E.B. Cowling, E. Gorhann and W.W. McFee, 1978. National Atmospheric Deposition Program NC-141, A Report To The Council On Environmental Quality.

Hales, J.M. and M. Terry Dana, 1979. Regional Scale Deposition Of Sulphur Dioxide By Precipitation Scavenging, Atmos. Envir. 13, 1121-1132.

Henmi, T. and E.R. Reiter, 1978. Regional Residence Time Of Sulphur Dioxide Over The Eastern United States, Atmos. Envir., 12, 1489-1496.

Intensive Sulphate Study, Aug., 1976. Preliminary Report of The Intensive Sulphate Study, August, 1976, Ed. D.M. Whelpdale, Atmospheric Environment Service, 4905 Dufferin Street, Downsview, Ontario.

Maul, P.R., 1978. Preliminary Estimates Of The Washout Coefficient For Sulphur Dioxide Using Data From An East Midlands Ground Level Monitoring Network, Atmos. Envir., 12, 2515-2517.

McMahon, T.A., P.J. Denison and R. Fleming, 1976. A Long-Distance Air Pollution Transportation Model Incorporating Washout And Dry Deposition Components, Atmos. Envir.,10, 751-761.

NATO Advanced Research Institute, 1978. The Effect of Precipitation On Terrestrial Ecosystems. Proc. Symposium, Toronto, Canada (in press).

Shannon, J.D., 1979. The Advanced Statistical Trajectory Regional Air Pollution Model, Proc. 4th Symp. On Turbulence, Diffusion And Air Pollution, Reno, Nevada, Jan. 1979. Sponsor Amer. Met. Soc.

Slinn, W.G.N., L. Hasse, B.B. Hicks, A.W. Hogan, D. Lal, P.S. Liss, K.O. Munnich, G.A. Sehmel and O. Vittori, 1978. Some aspects of the transfer of atmospheric trace constituents past the air-sea interface, Atmos. Envir., 12, 2055-2089.

Voldner, E.C., 1979. Personal communication based on Canadian LRTAP SO_2 Emission Inventory.

Voldner, E.C., M.P. Olson, K. Oikawa and M. Loiselle, 1979. Comparison Between Measured and Computed Concentrations Of Sulphur Compounds In Eastern North America, Proc. Of CAGP Symp. On The Budgets and Cycles Of Trace Gases And Aerosols In The Atmosphere, 12-18 Aug., Boulder, Colorado. (to be published in J. of Geo. Res).

TABLE CAPTIONS

1. The temperature dependence of the Henry's constant K_H, the first dissociation constant K_1 and their product K_1K_H for an SO_2-air-water system.

2. The correlation between observed hydrogen and sulphate ion concentrations (μmole ℓ^{-1}) in monthly rain samples at 25 CANSAP sites for May to September 1977 and 1978 (refer to Figure 4 for site locations using the number in the left hand column).
$[H^+]_r^{obs} = A + B\ [SO_4^=]_r^{obs}$

3. The correlation between hydrogen and sulphate ion concentrations (μmole ℓ^{-1}) for event rain samples at four MAP3S sites for May to September 1977 and 1978 (refer to Figure 4 for site location using the number in the left hand column). $[H^+]_r^{obs} = A + B\ [SO_4^=]_r^{obs}$

FIGURE CAPTIONS

1. The dependence of the washout ratio of SO_2 by rain on pH for two temperatures, 0 and 25 C, under equilibrium scavenging conditions (the hatched area represents those situations commonly encountered in the atmosphere).

2. The computed fraction of total hydrogen ions in wet deposition that are contributed by dissolved SO_2, f, as a function of sulphur dioxide concentration for various aerosol sulphate concentrations (I, II and III correspond to 1, 10 100 $\mu g\text{-}SO_4^{=}\ m^{-3}$, respectively) and for two temperatures 0C (solid line) and 25C (dashed line).
$W_{SO_4} = 5 \times 10^5$ $\underline{B = 2}$

3. The computed fraction of total hydrogen ions in wet deposition that are contributed by dissolved SO_2, f, as a function of sulphur dioxide concentration for various aerosol sulphate concentrations (I,II and III correspond to 1, 10 and 100 $\mu g\text{-}SO_4^{=}\ m^{-3}$, respectively) and for two temperatures 0C (solid line) and 25 C (dashed line).
$W_{SO_4} = 5 \times 10^5$ $\underline{B = 1}$

4. The location of CANSAP (circles) and MAP3S (squares) sites for which correlations between hydrogen and sulphate ions in rain were computed (Tables 2 and 3, respectively).

5. The correlation coefficient R between hydrogen and sulphate ions in rain samples collected between May and September, 1977 and 1978. The number of samples are in brackets. The R-value is underlined if the correlation is significant at

the 1% level.

6. Isolines of sulphur dioxide emission rates (10^6 kg y^{-1}) in eastern North America for 1975, (Voldner, 1979)

7. The slope B and intercept A if significant (in brackets) for the linear correlation $[H^+]_r^{obs} = A + B\ [SO_4^=]_r^{obs}$ in rain samples between May and September 1977 and 1978. Values are plotted for those sites having a significant correlation at the 1% level.

8. Computed pH of rain as a function of sulphate aerosol concentration for various sulphur dioxide air concentrations ($\mu g\ m^{-3}$) and for OC, $W_{SO_4} = 5 \times 10^5$ and B = 2. The dashed line corresponds to the case with no sulphur dioxide present.

9. Computed pH of rain as a function of sulphate aerosol concentration for various sulphur dioxide air concentrations ($\mu g\ m^{-3}$) and for OC, $W_{SO_4} = 5 \times 10^5$, and B = 1. The dashed line corresponds to the case with no sulphur dioxide present.

Table 1

The temperature dependence of the Henry's constant K_H, the first dissociation constant K_1 and their product $K_1 K_H$ for an SO_2-air-water system.

TEMPERATURE (C)	K_H (mole l_r^{-1}/mole l_{air}^{-1})	K_1 (mole l_r^{-1})	$K_1 K_H$ (mole l_r^{-1})^2/(mole l_a^{-1})
0	73.5	3.1×10^{-2}	2.3
15	41.5	2.2×10^{-2}	0.91
25	30.3	1.7×10^{-2}	0.53

Table 2

The correlation between hydrogen and sulphate ion concentrations (μ mole l^{-1}) in monthly rain samples at 25 CANSAP sites for May to September 1977 and 1978 (refer to Figure 4 for site locations using the number in the left hand column) $[H^+]_r^{obs} = A + B\,[SO_4^=]_r^{obs}$

STATION	$[H^+]_r^{obs}$ RANGE* (μ mole l)	A INTERCEPT (μ mole l^{-1})	B SLOPE	CORR. COEFF. R	NUMBER OF MONTHLY DATA
1 Trout Lake	0.12 - 2.4	1.25	-.03	-.39	9
2 Pickle Lake	0.7 - 11	1.1	0.30	0.51	10
3 Atikokan	2.2 - 24	-4.3	0.90	0.66	10
4 Moosonee	0.2 - 9.0	1.1	.025	0.68	8
5 Wawa	16 - 55	-4.3	1.17	0.89	6
6 Windsor	0.35 - 97	-53	1.13	0.62	8
7 Simcoe	9.6 - 45	11.0	0.42	0.44	6
8 Mt. Forest	0.43 - 64	-27.0	.94	0.54	8
9 Peterborough	6.9 - 84.	-8.6	1.13	0.85	8
10 Kingston	4.1 - 56	17.9	.18	0.18	9
11 Maniwaki	17 - 67	0.86	1.07	0.76	9
12 St. Hubert	50 - 91	-3.4	.92	0.82	6
13 Quebec City	2.5 - 94	1.68	.91	0.48	9
14 Chibougamau	8.5 - 48	1.59	1.24	0.99	7
15 Nitchiquon	1.2 - 19	-0.25	0.98	0.93	7
16 Fort Chimo	1.0 - 9.8	-0.49	.64	0.70	8
17 Sept-Iles	2.4 - 70	0.89	1.27	0.96	9
18 Goose	6.1 - 14.8	0.11	1.27	0.97	5
19 Charlo	4.4 - 35	7.1	.66	0.71	7
20 St. John, N.B.	1.0 - 83	3.16	.95	0.76	9
21 Shelburne	14 - 53	6.4	1.0	0.81	10

CONTINUED

Table 2 - (Continued)

STATION	$[H^+]_r^{obs}$ RANGE* (μ mole 1)	A INTERCEPT (μ mole 1^{-1})	B SLOPE	CORR. COEFF. R	NUMBER OF MONTHLY DATA
22 Truro	3.4 - 39	-.59	1.31	0.97	10
23 Sable Island	1.9 - 70	-13	1.07	0.89	7
24 Stephenville	14 - 57	-4.4	1.1	0.87	9
25 Gander	6 - 23	3.99	0.77	0.80	10

! May 77 sample discarded - abnormally high calcium.

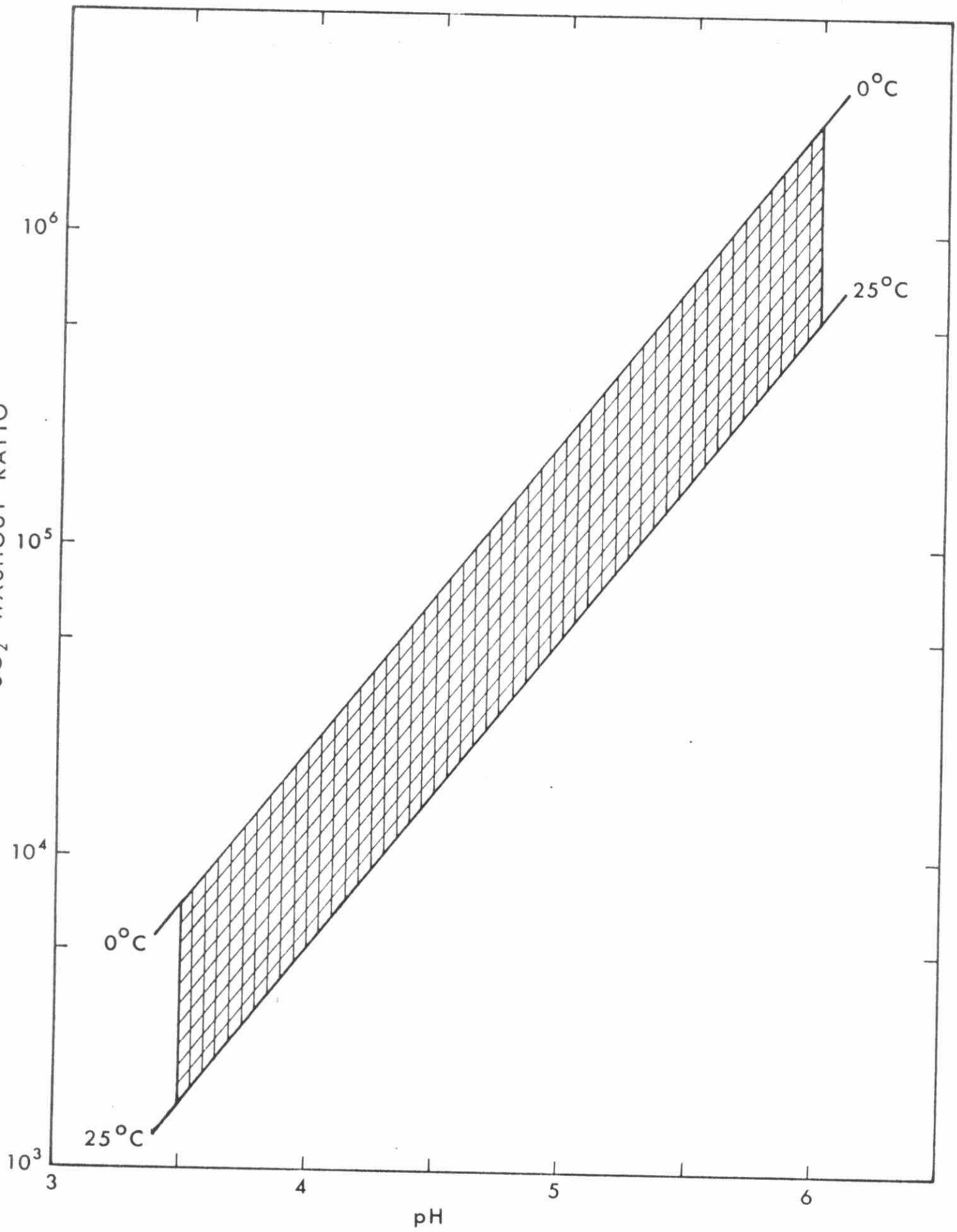
* $pH = -\log_{10} [H^+]_r$

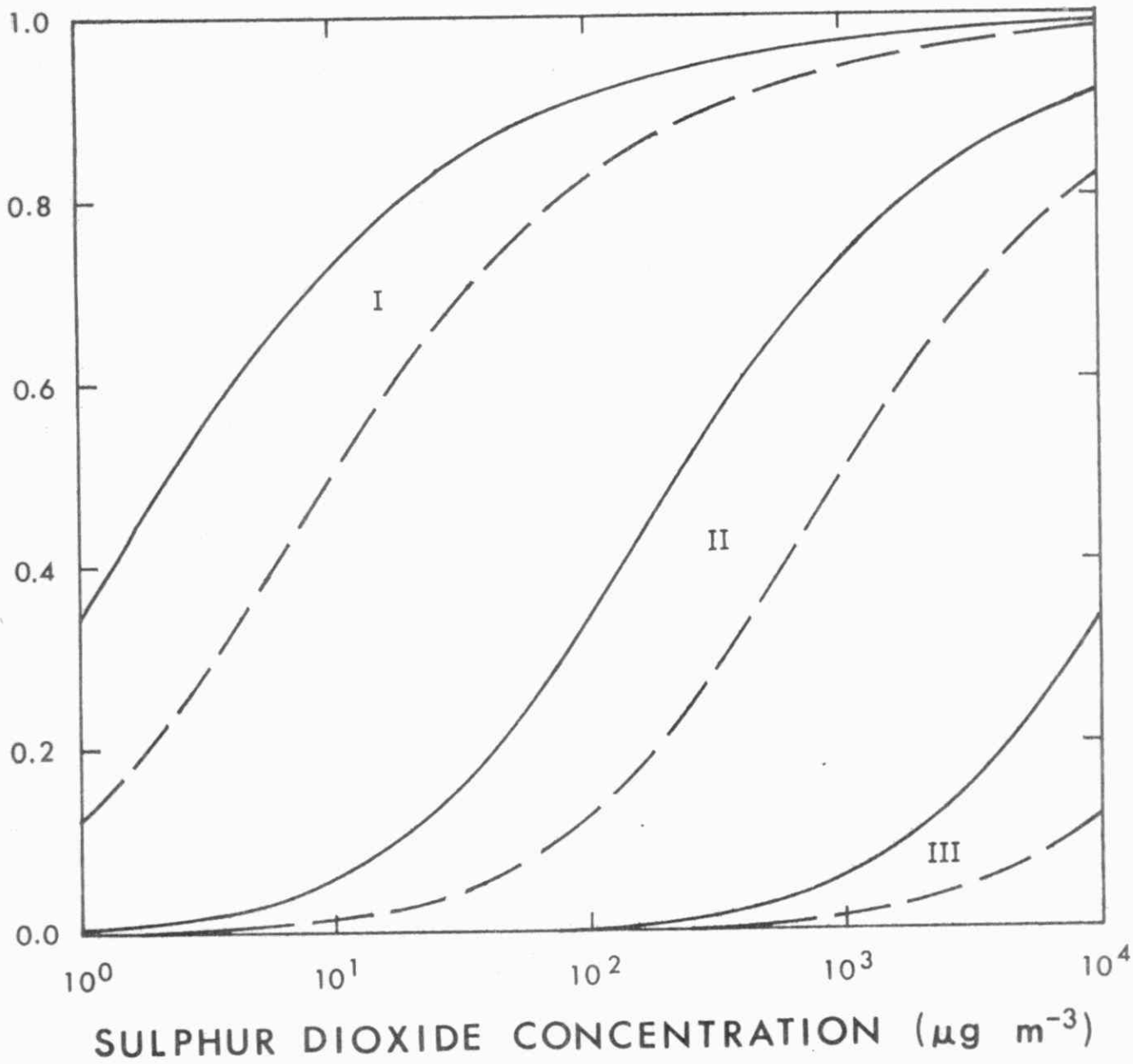
Table 3

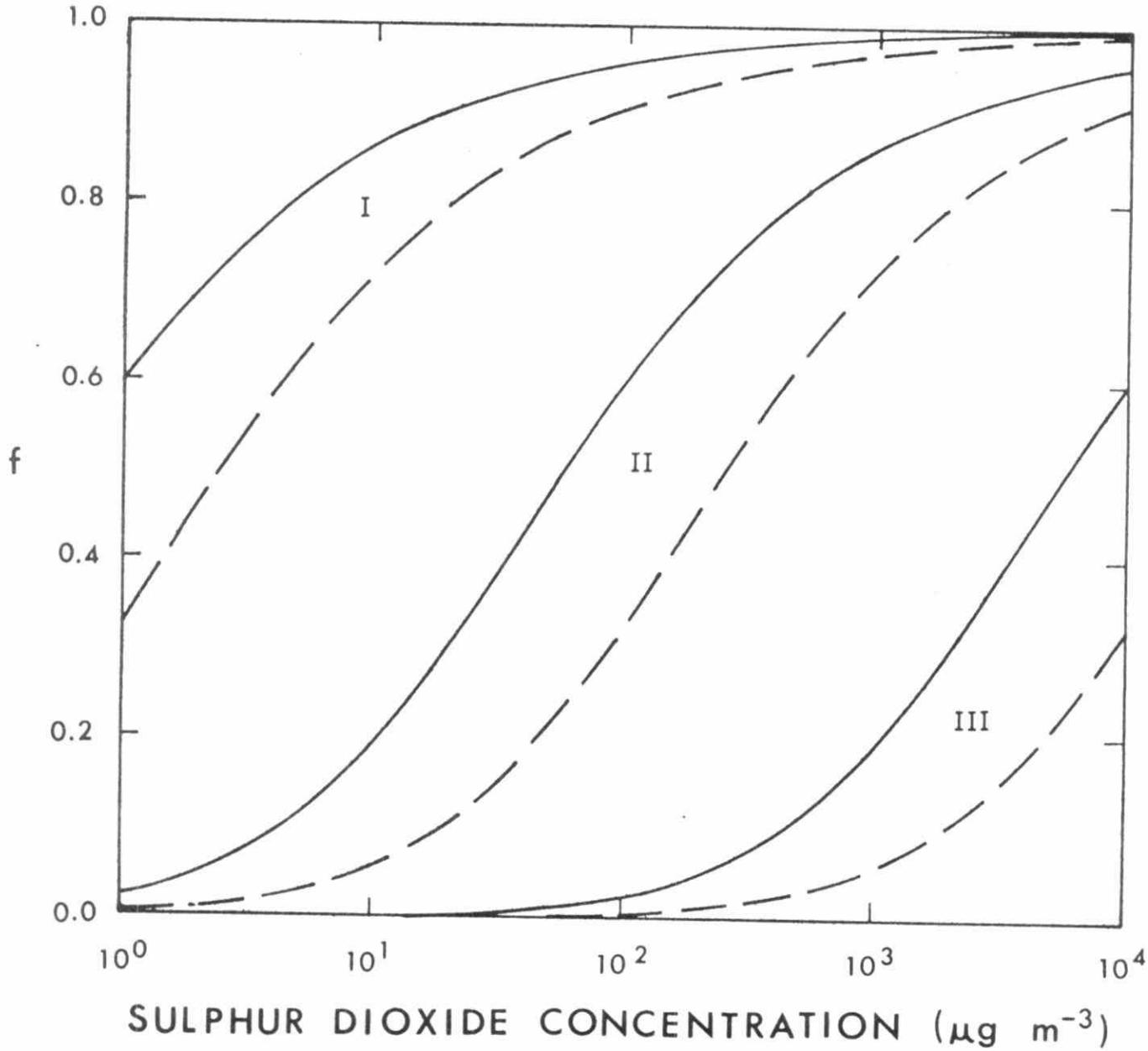
The correlation between hydrogen and sulphate ion concentrations (μ mole l^{-1}) for event rain samples at four MAP3S sites for May to September 1977 and 1978 (refer to Figure 4 for site location using the number in the left hand column) $[H^+]_r^{obs} = A + B\,[SO_4^=]_r^{obs}$.

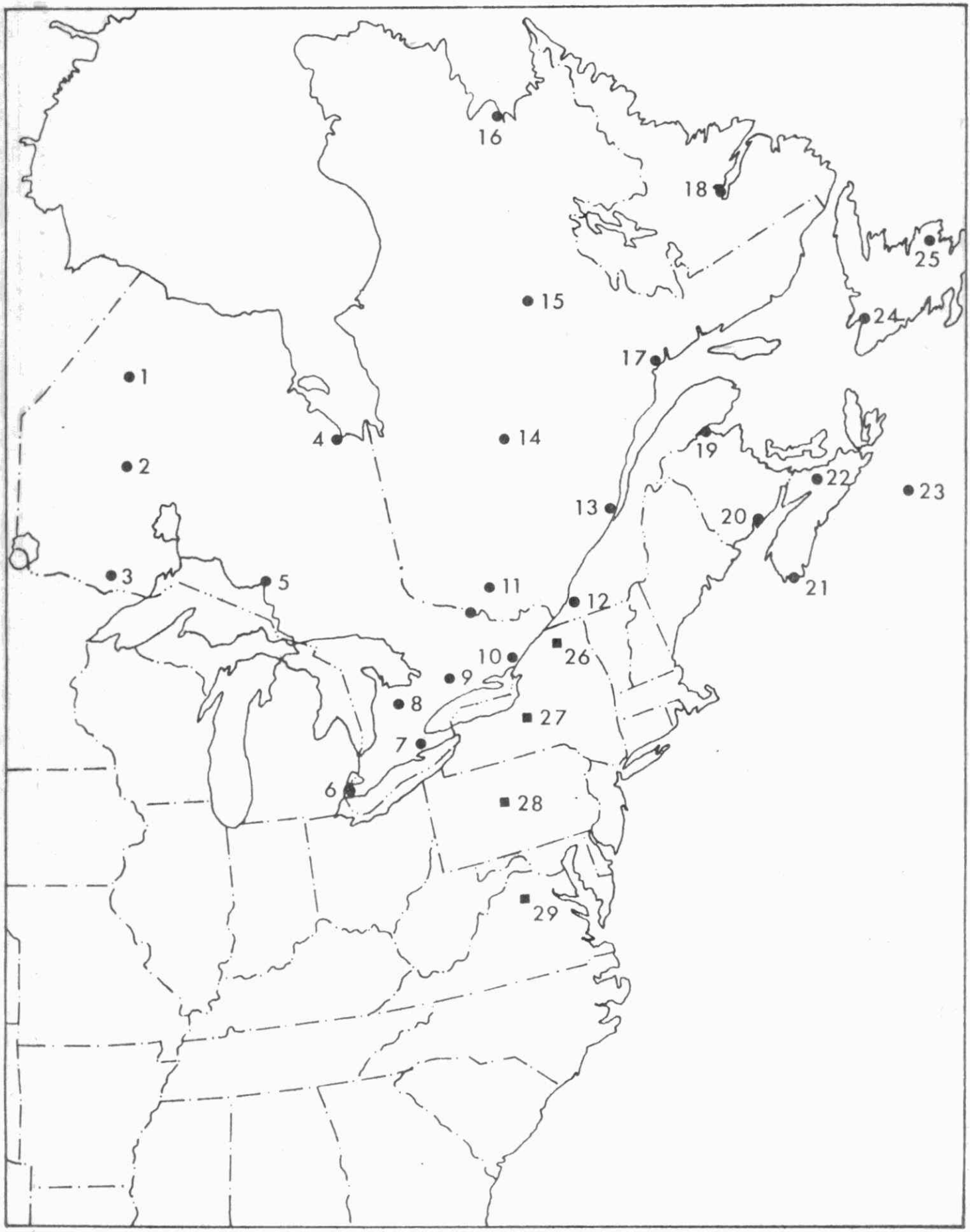
STATION	$[H^+]_r$ RANGE* (μ mole l^{-1})	INTERCEPT A (μ mole l^{-1})	SLOPE B	CORR. COEFF. R	NUMBER OF EVENT SAMPLES
26 WHITEFACE MT. N.Y.	14 - 200	9.2	1.7	0.89	59
27 ITHICA, N.Y.	21 - 350	28	1.6	0.95	39
28 PENN STATE	35 - 280	6.8	2.1	0.98	53
29 VIRGINIA	19 - 380	8.0	1.8	0.96	44

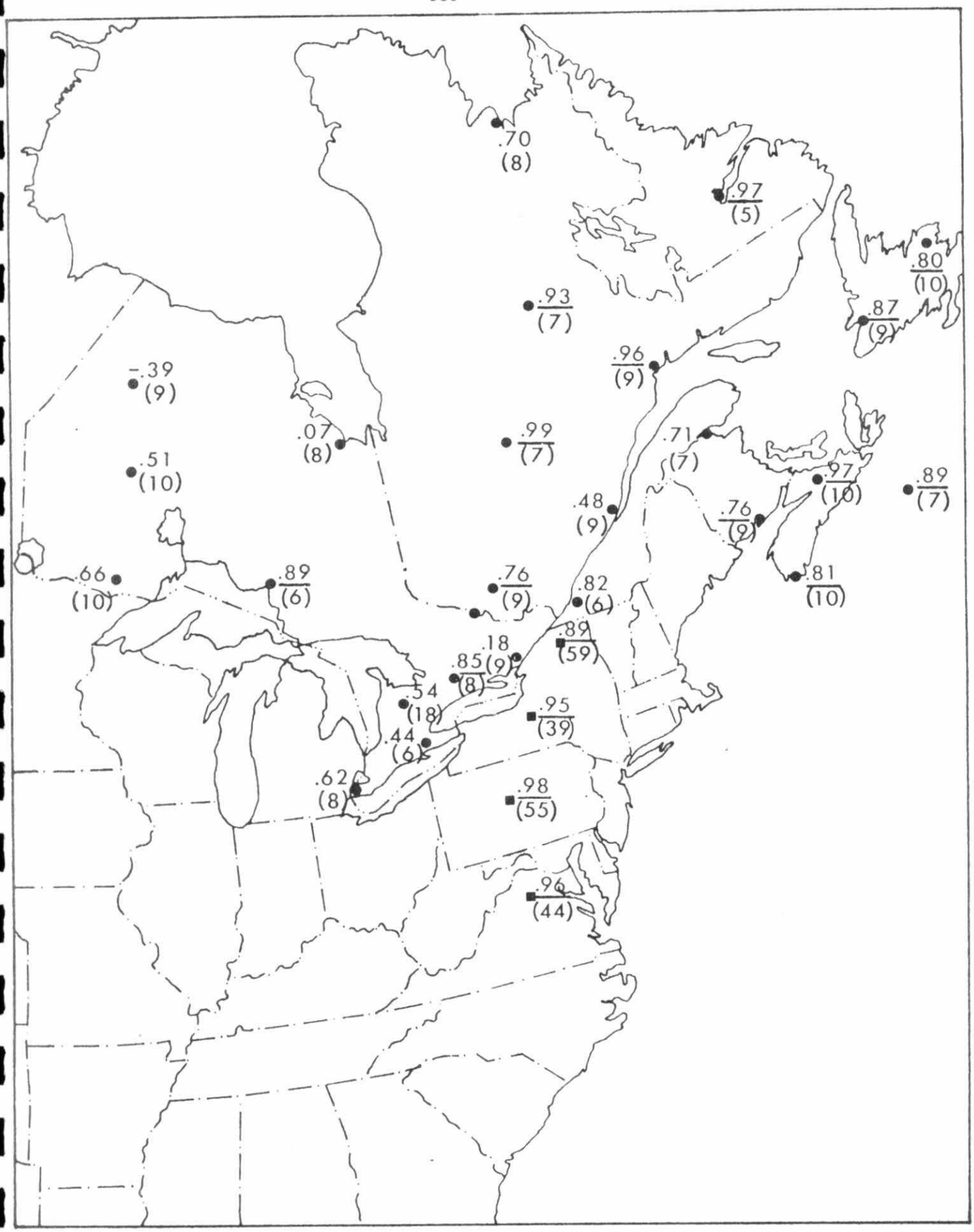
* $pH = -\log_{10} [H^+]_r$

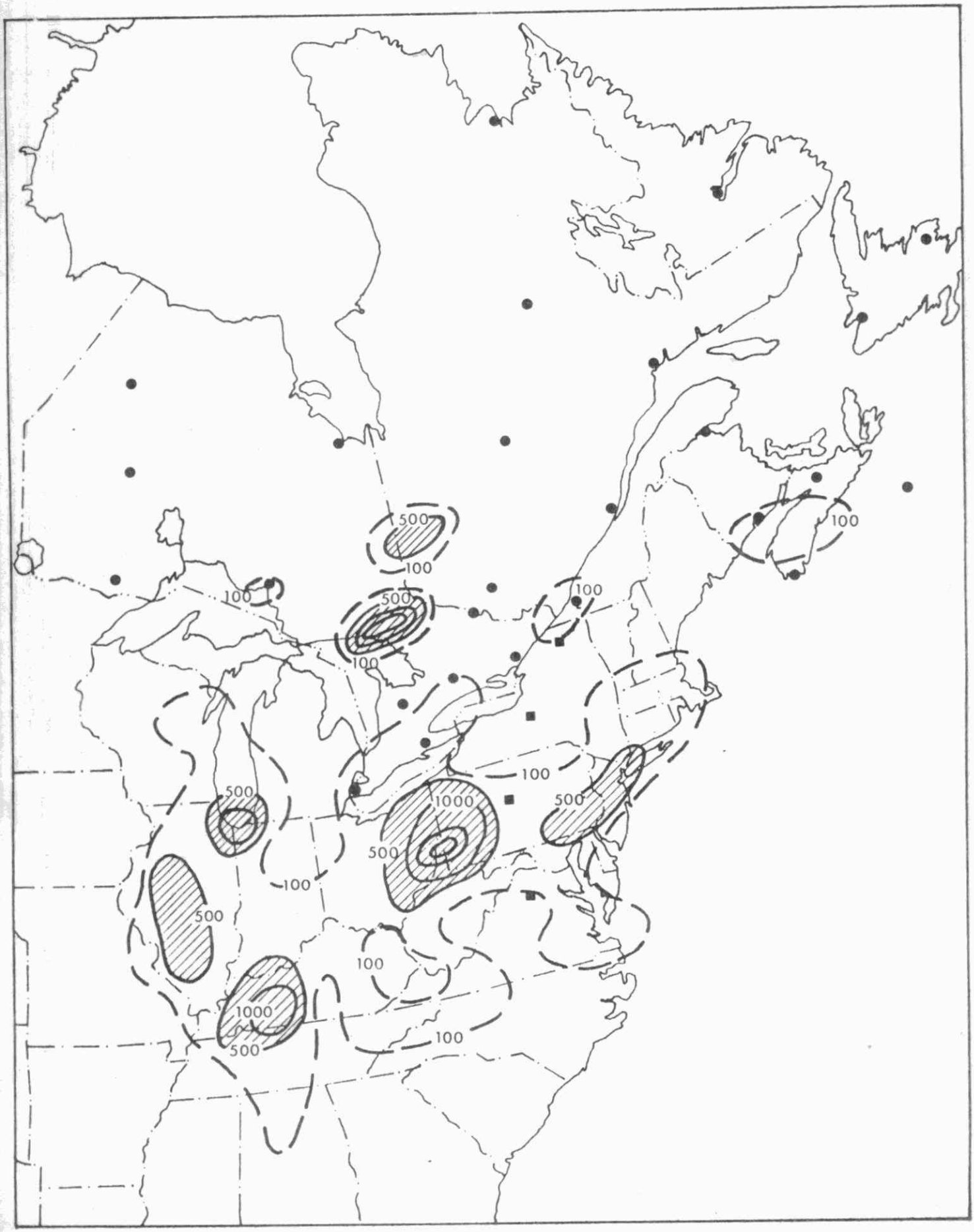

0°C
25°C
0°C
25°C
10^6
10^5
10^4
10^3
SO_2 WASHOUT RATIO
3
4
5
6
pH

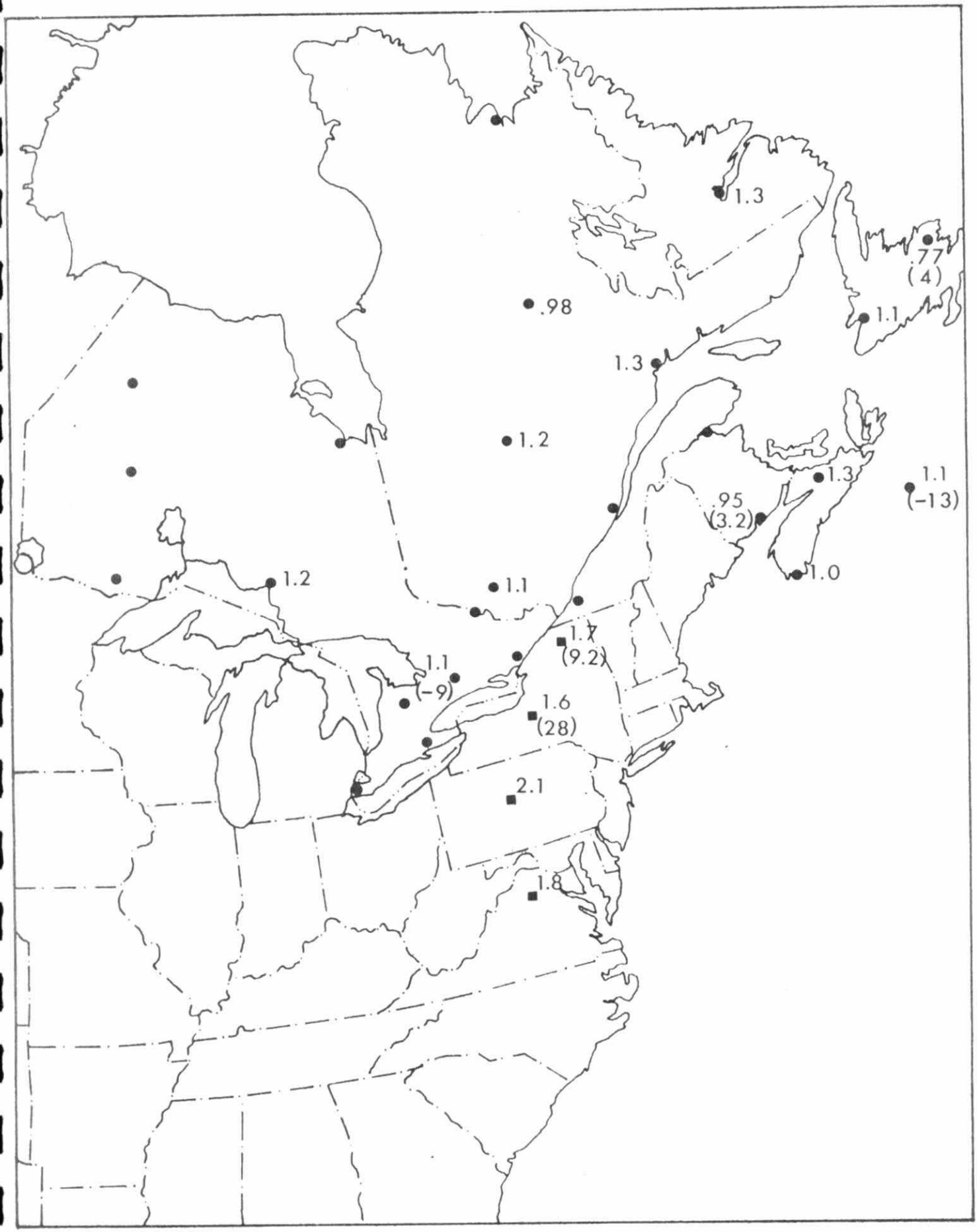

1.0
0.8
0.6
0.4
0.2
0.0
f
I
II
III
10^0
10^1
10^2
10^3
10^4
SULPHUR DIOXIDE CONCENTRATION (μg m^{-3})

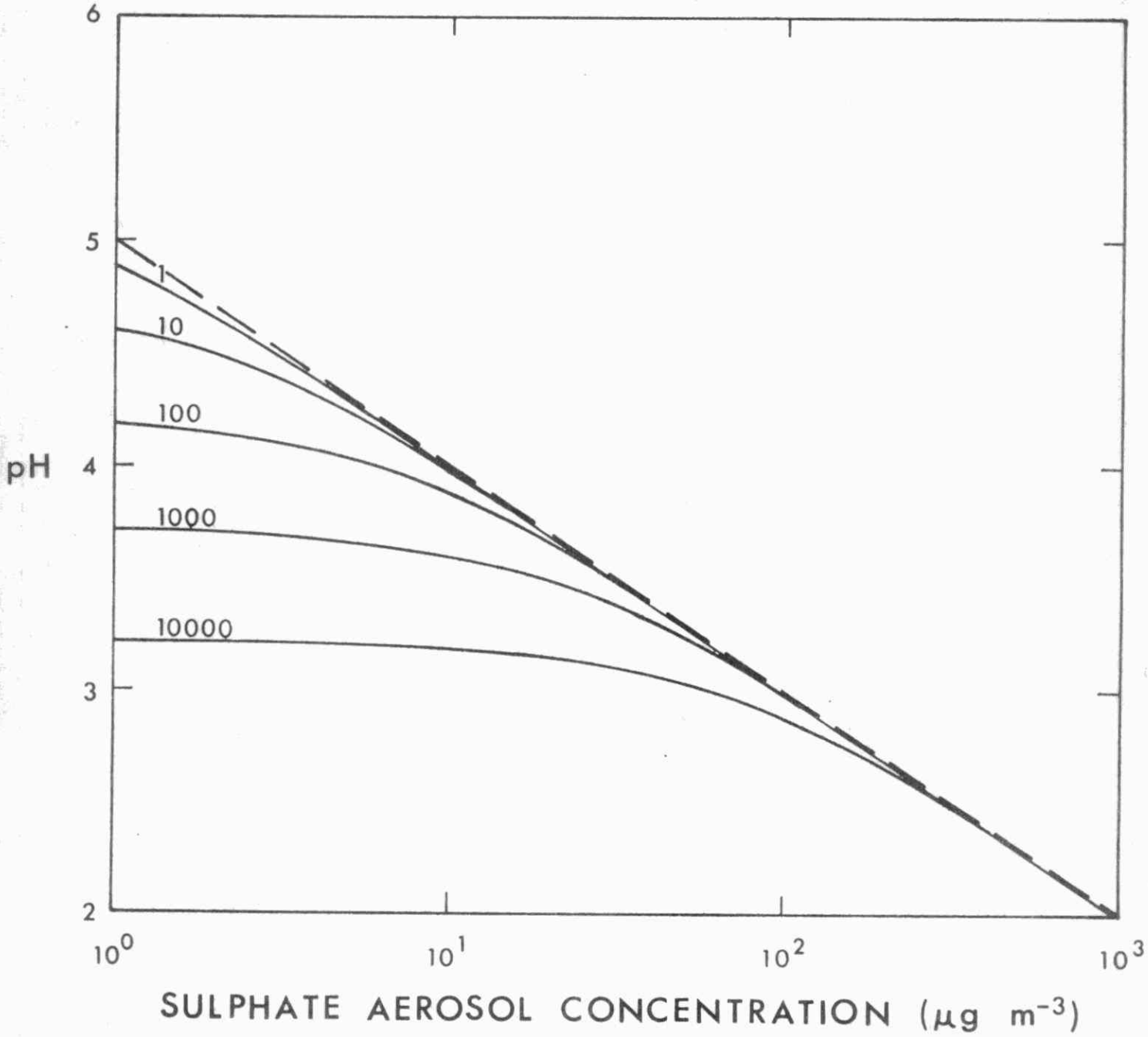

1.0
0.8
0.6
0.4
0.2
0.0
f
I
II
III
10^0
10^1
10^2
10^3
10^4
SULPHUR DIOXIDE CONCENTRATION (μg m^{-3})

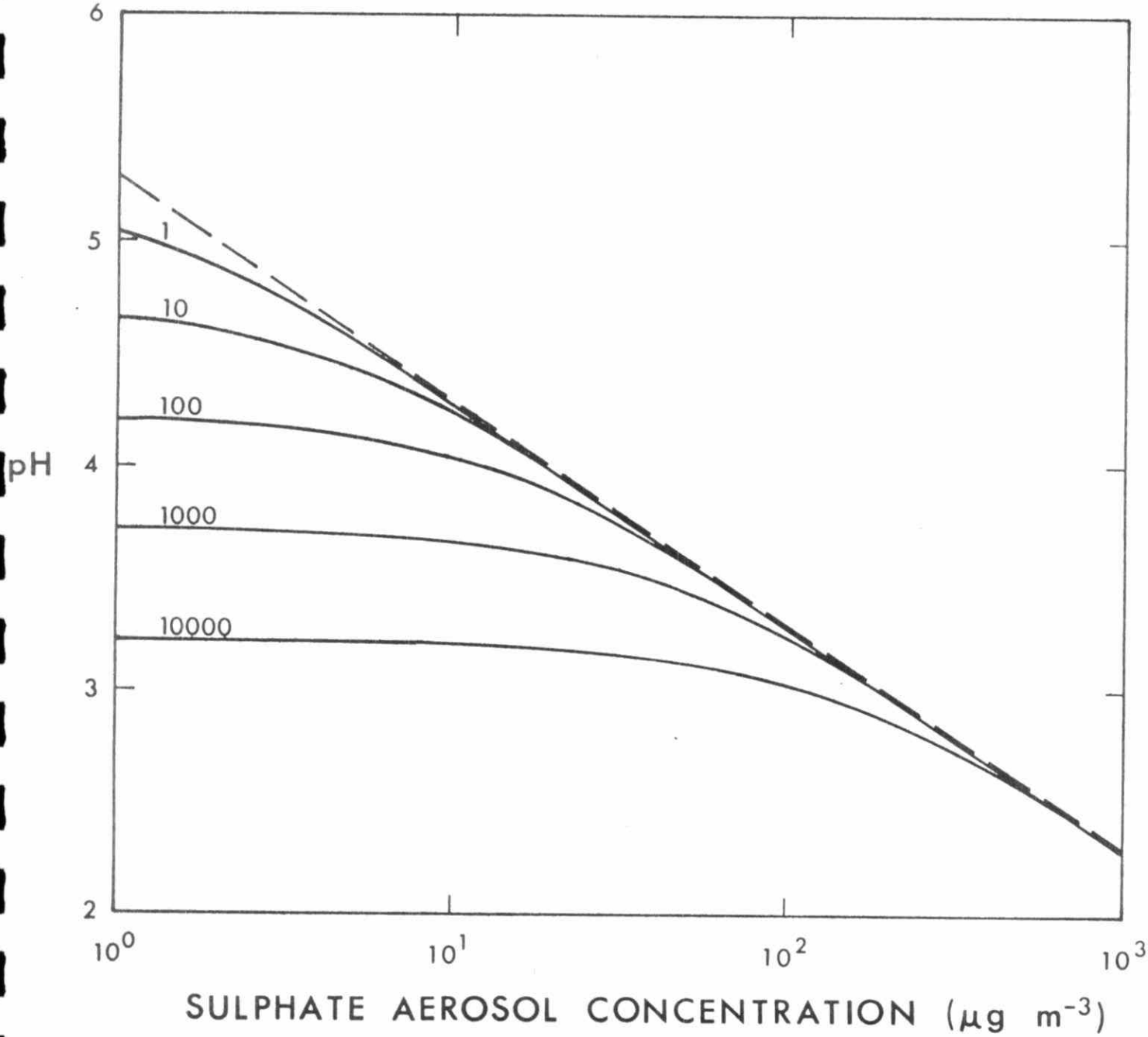

16
18
25
15
24
17
1
4
14
19
2
22
23
13
20
3
5
11
12
21
10
26
9
8
27
7
6
28
29


.70 (8)
.97 (5)
.80 (10)
.93 (7)
.87 (9)
.96 (9)
.39 (9)
.07 (8)
.99 (7)
.71 (7)
.51 (10)
.97 (10)
.89 (7)
.48 (9)
.76 (9)
.66 (10)
.89 (6)
.76 (9)
.82 (6)
.81 (10)
.89 (59)
.18 (9)
.85 (8)
.54 (18)
.95 (39)
.44 (6)
.62 (8)
.98 (55)
.96 (44)


500
100
100
500
100
100
100
500
1000
500
500
100
500
100
1000
500
100


1.3
.77
(4)
.98
1.1
1.3
1.2
1.3
1.1
(-13)
95
(3.2)
1.2
1.1
1.0
1.7
(9.2)
1.1
(-9)
1.6
(28)
2.1
1.8


6
5
4
3
2
pH
1
10
100
1000
10000
10^0
10^1
10^2
10^3
SULPHATE AEROSOL CONCENTRATION ($\mu g\ m^{-3}$)

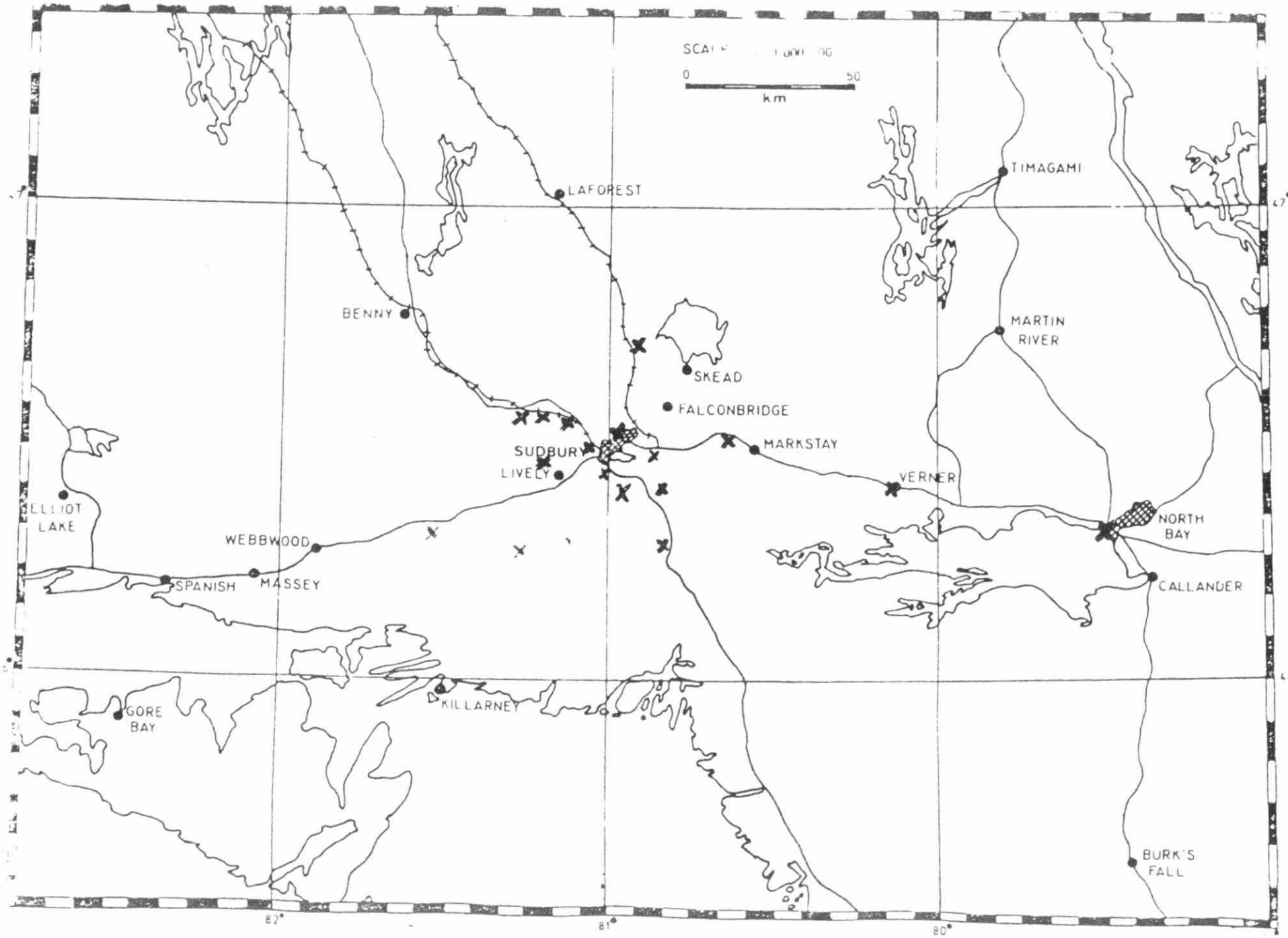

6
5
4
3
2
pH
1
10
100
1000
10000
10^0
10^1
10^2
10^3
SULPHATE AEROSOL CONCENTRATION ($\mu g\ m^{-3}$)

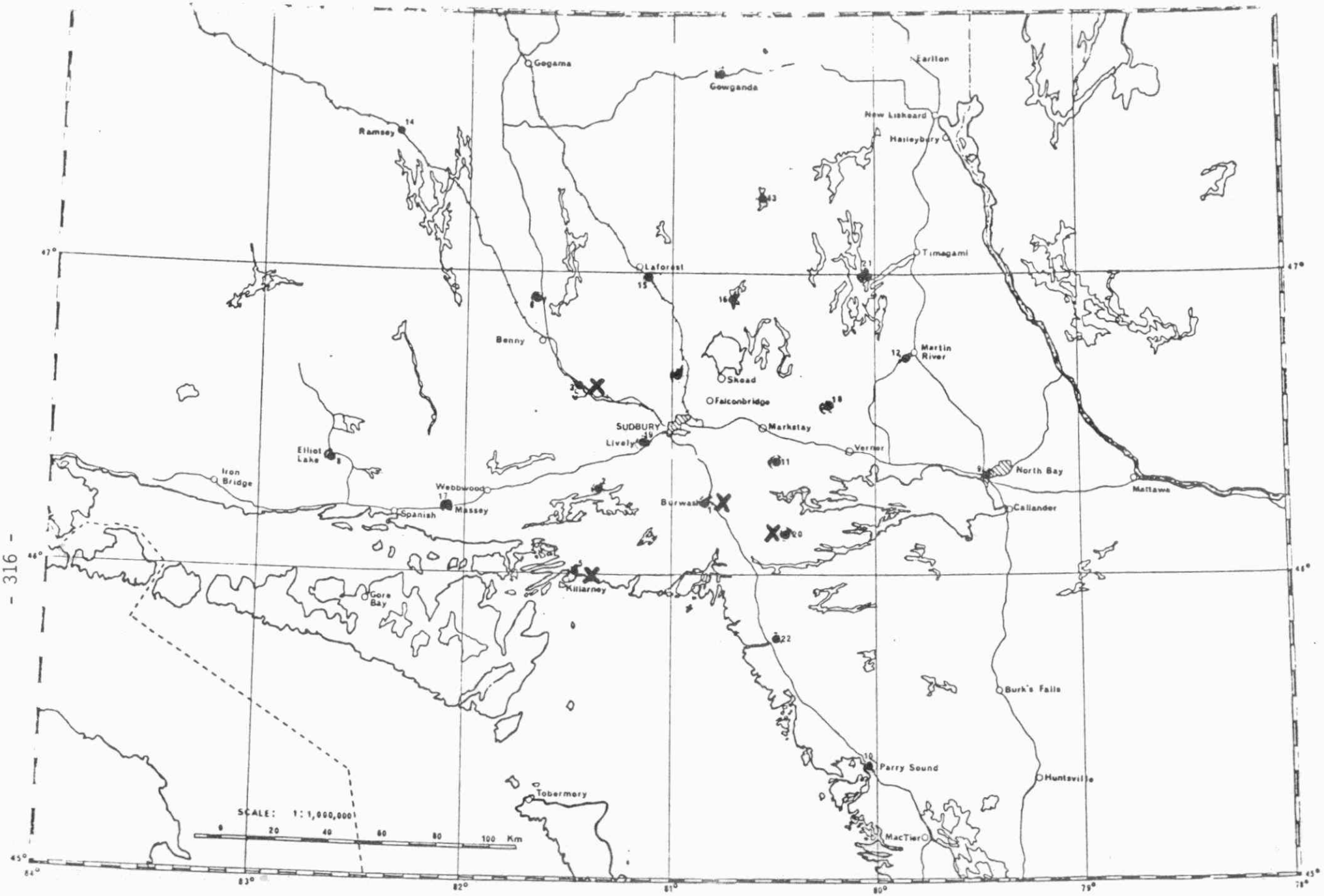
APPENDIX EIGHT

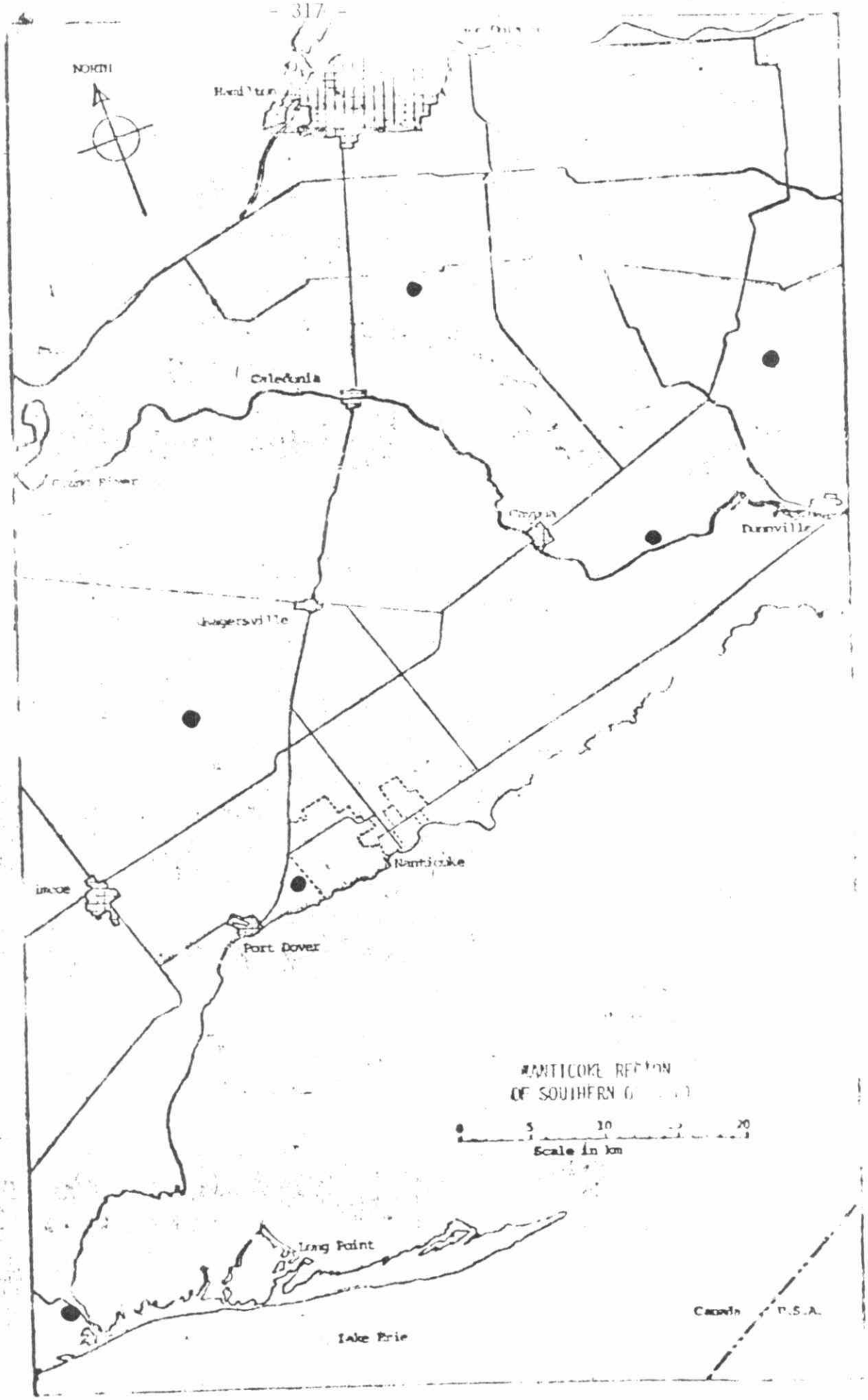
PROVINCIAL ACID PRECIPITATION DEPOSITION NETWORK

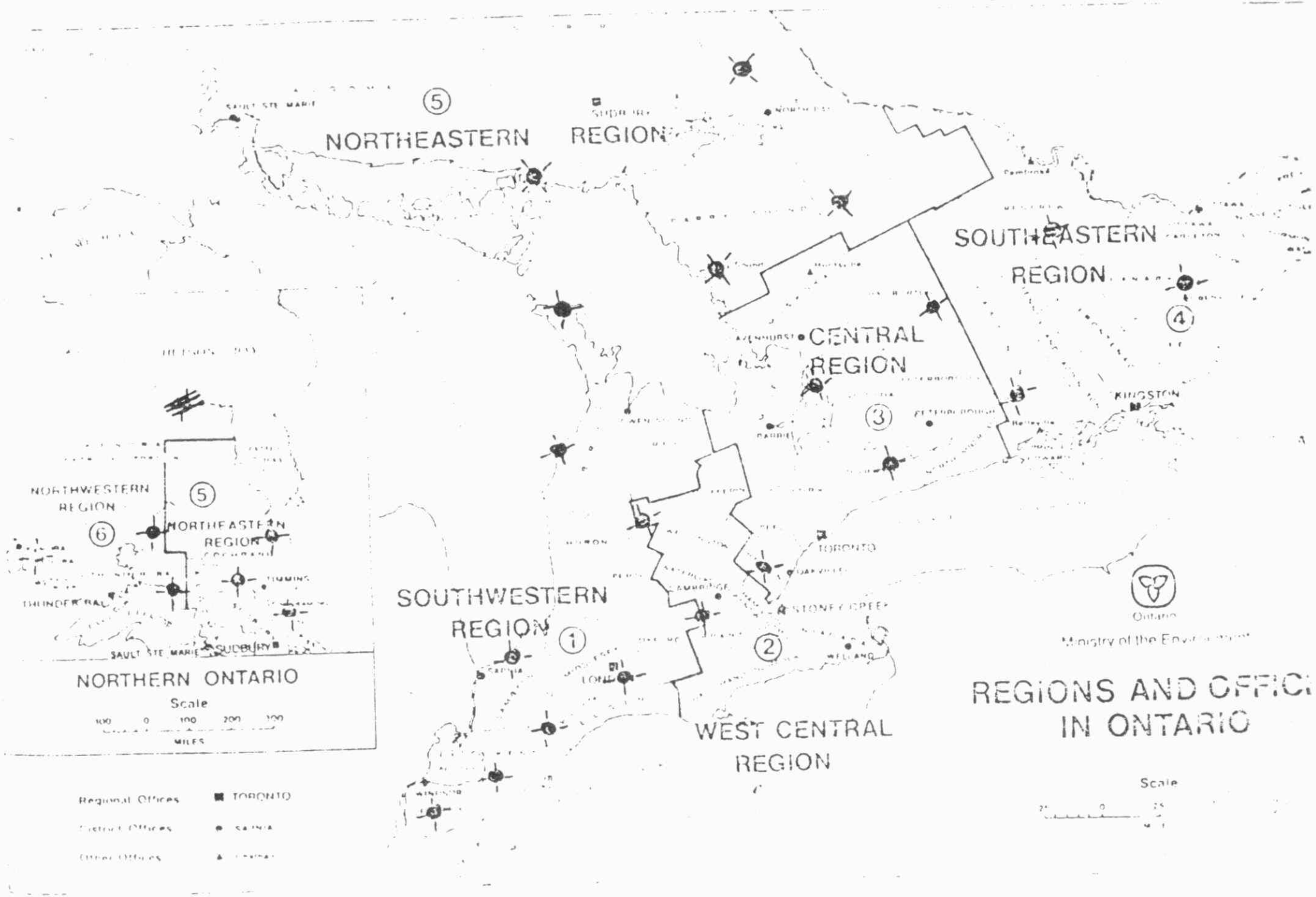
Maris Lusis

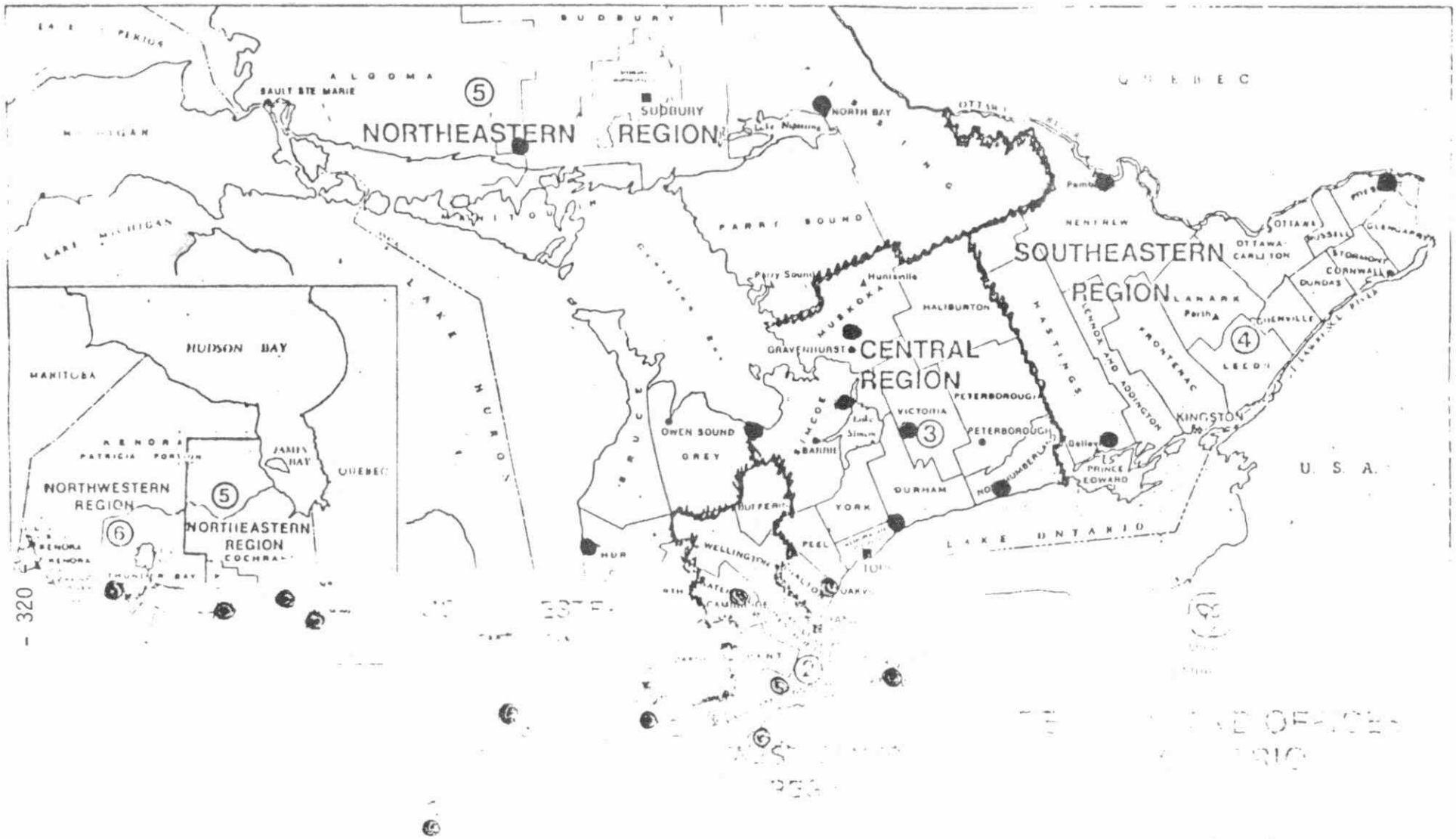
Included in this appendix are related figures and diagrams as well as a schedule of events for completion.

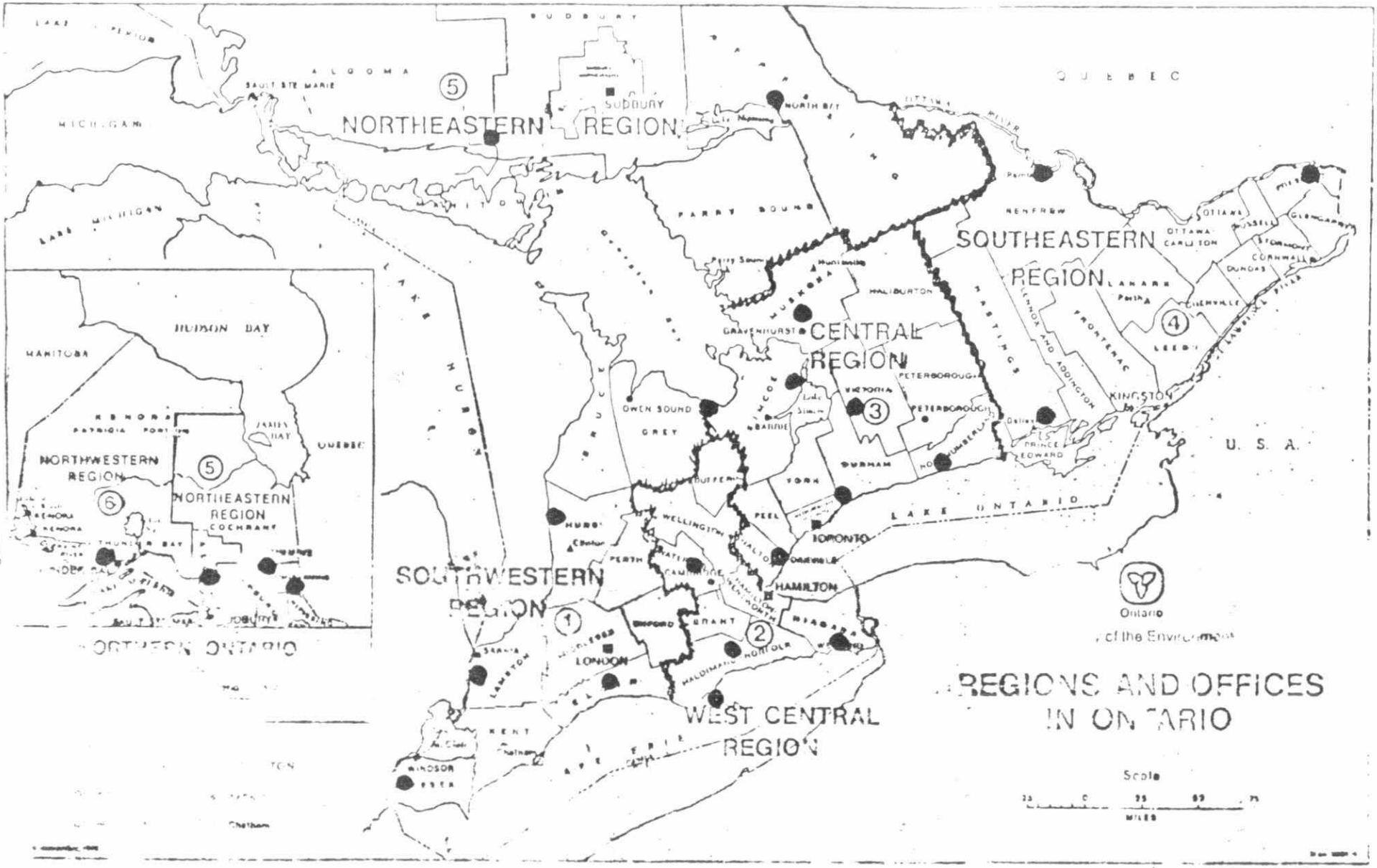

SCALE 1:1 000 000
0
50
km
TIMAGAMI
LAFOREST
BENNY
MARTIN RIVER
SKEAD
FALCONBRIDGE
SUDBURY
MARKSTAY
LIVELY
VERNER
ELLIOT LAKE
NORTH BAY
WEBBWOOD
SPANISH
MASSEY
CALLANDER
KILLARNEY
GORE BAY
BURK'S FALL
47°
46°
82°
81°
80°


Gogama
Gowganda
Earlton
New Liskeard
Haileybury
Ramsey
Timagami
Laforest
Benny
Martin River
Skead
Falconbridge
SUDBURY
Markstay
Lively
Verner
Elliot Lake
Iron Bridge
Webbwood
Massey
Spanish
Burwash
North Bay
Mattawa
Callander
Killarney
Gore Bay
Burk's Falls
Parry Sound
Huntsville
Tobermory
MacTier
SCALE: 1:1,000,000
0 20 40 60 80 100 Km
47°
46°
45°
84°
83°
82°
81°
80°
79°
78°

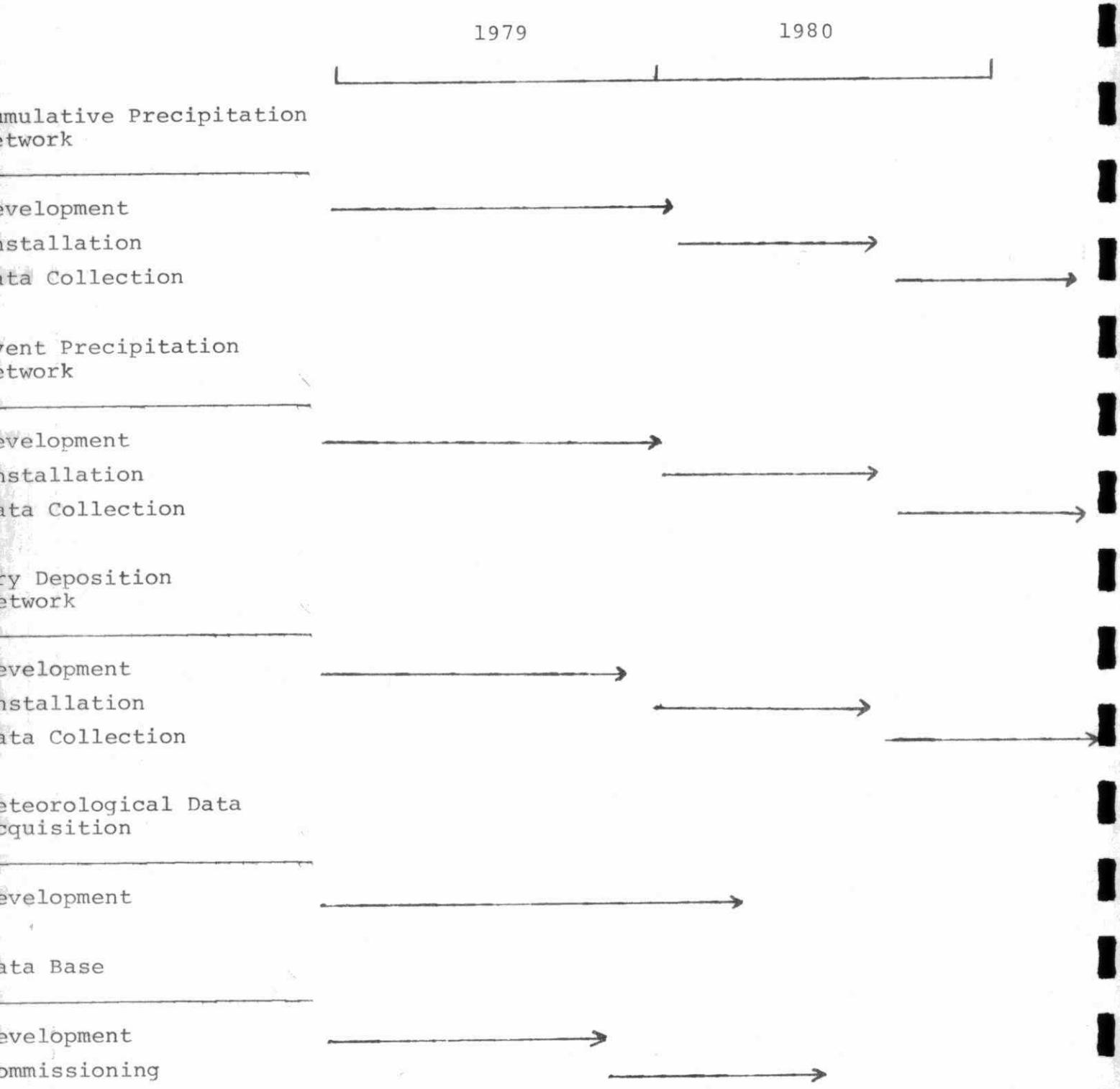

NORTH
Caledonia
Dunnville
Nanticoke
Port Dover
Long Point
Lake Erie
Scale in km


⑤
NORTHEASTERN REGION
SOUTHEASTERN REGION
④
CENTRAL REGION
③
KINGSTON
TORONTO
SOUTHWESTERN REGION
①
②
WEST CENTRAL REGION
NORTHWESTERN REGION
⑥
⑤
NORTHEASTERN REGION
SAULT STE MARIE
SUDBURY
NORTHERN ONTARIO
Scale
100 0 100 200 300
MILES
Regional Offices
TORONTO
SARNIA
REGIONS AND OFFIC
IN ONTARIO
Scale


NORTHEASTERN REGION
SOUTHEASTERN REGION
CENTRAL REGION
NORTHWESTERN REGION
NORTHEASTERN REGION
HUDSON BAY
SUDBURY
SAULT STE MARIE
NORTH BAY
PARRY SOUND
HALIBURTON
OWEN SOUND
GREY
PETERBOROUGH
KINGSTON
LANARK
LEEDS
OTTAWA-CARLETON
DURHAM
YORK
PEEL
LAKE ONTARIO
LAKE HURON
LAKE MICHIGAN
QUEBEC
U. S. A.
MANITOBA
ONTARIO


NORTHEASTERN REGION
5
SUDBURY
SAULT STE MARIE
ALGOMA
MICHIGAN
LAKE SUPERIOR
LAKE MICHIGAN
HUDSON BAY
MANITOBA
ONTARIO
QUEBEC
NORTH B/T
PARRY SOUND
HALIBURTON
HUNTSVILLE
GRAVENHURST
CENTRAL REGION
3
PETERBOROUGH
VICTORIA
SOUTHEASTERN REGION
4
RENFREW
OTTAWA CARLETON
LANARK
LEEDS
KINGSTON
PRINCE EDWARD
LENNOX AND ADDINGTON
FRONTENAC
HASTINGS
U. S. A.
LAKE ONTARIO
OWEN SOUND
GREY
BARRIE
SIMCOE
DURHAM
YORK
PEEL
TORONTO
OAKVILLE
HAMILTON
WELLINGTON
PERTH
SOUTHWESTERN REGION
1
LONDON
OXFORD
BRANT
2
WEST CENTRAL REGION
KENT
LAMBTON
WINDSOR
ESSEX
LAKE ERIE
NORTHWESTERN REGION
6
THUNDER BAY
KENORA
PATRICIA PORTION
NORTHEASTERN REGION
COCHRANE
JAMES BAY
QUEBEC
NORTHERN ONTARIO
Ontario
of the Environment
REGIONS AND OFFICES IN ONTARIO
Scale
MILES

TENTATIVE SCHEDULE



AUTHOR'S PROOF.

APPENDIX NINE

DEPOSITION OF NUTRIENTS AND MAJOR IONS BY PRECIPITATION IN SOUTH-CENTRAL ONTARIO

SCHEIDER
W. A. SCHNEIDER, W. R. SNYDER and B. CLARK
Ontario Ministry of the Environment, Limnology and Toxicity Section, Water Resources Branch, Box 213, Rexdale, Canada M9W 5L1

(Received 23 February, 1979; revised 9 June, 1979)

Abstract. As part of a study of the substance budgets of lakes in south-central Ontario, a network of precipitation collectors (8 bulk, 7 wet only) was operated to measure the deposition of nutrients and major ions. Results are reported for total P, total Kjeldahl N, NO_3^--N, NH_4^+-N, total N, Fe, H^+, Ca^{++}, Mg^{++}, Na^+, K^+, $SO_4^=$ and CL^- for a two year period (August 1976–July 1978). On an equivalent basis the dominant anion in both bulk and wet precipitation was $SO_4^=$, with H^+ the dominant cation. Precipitation in the study area is more acidic than that analyzed at any other location on the Canadian Shield to date. Concentrations of ions varied by 1 to 3 orders of magnitude between individual precipitation events and annual deposition varied by as much as 2-fold in the two years of study. Annual wet deposition contributed > 60% of bulk deposition for all substances except total P. Seasonal trends in deposition with summer maxima were noted for most ions. For Harp Lake, a small Precambrian Lake with a lake area of 12.7% of its total drainage area, precipitation input directly to the lake surface was an important source of nutrients and major ions. This was especially the case for P, N and H^+ because these substances were retained by the terrestrial drainage basin.

12.6 %

1. Introduction

Excluding anthropogenic, point-source inputs, nutrients and major ions can enter lakes from terrestrial drainage, precipitation, lake sediments, or by direct gaseous transport from the atmosphere (reviewed by Gorham, 1961). In areas underlain by the granitic rocks of the Canadian Shield, weathering rates are low because of the resistant nature of the bedrock. Consequently, inputs to lakes by precipitation may assume greater relative importance. The majority of the studies which have considered precipitation as a source of input into lakes have concerned P (Dillon, 1974; Gomolka, 1975; Scheider, 1978 and others) because of its importance as an algal nutrient. Only Schindler and Nighswander (1970) and Schindler *et al.* (1976) have reported the relative importance of precipitation as a source of both major ions and nutrients to a lake with Canadian Shield drainage. Therefore, as part of a study on the material budgets of 15 lakes in south-central Ontario, we have measured the deposition of major ions and nutrients in precipitation at several locations for a two year period.

Wet precipitation is defined as the material collected during a rain or snow event and is useful in the consideration of the chemistry of rain or snow. Dry deposition includes particulate materials (soils, pollen) that settle by gravity, aerosols that are impacted onto earth surfaces and gases adsorbed on or by earth surfaces (Galloway and Likens, 1978). Both precipitation components act as material inputs to a lake. However, because of the difficulty in measuring the latter two fractions of dry deposition, our study deals only with wet and bulk precipitation. Bulk precipitation is operationally defined as that

which falls into a continuously open collector (Whitehead and Feth, 1964). It includes both wet precipitation and an unknown fraction of the particulate, aerosol and gaseous material that eventually reach the lake surface. If local contamination can be neglected, bulk precipitation probably better approximates what actually falls on the lake surface than does wet precipitation.

In this paper, we present concentrations and deposition rates of major ions and nutrients in bulk and wet precipitation. We investigate temporal patterns in deposition rates and obtain a preliminary indication of the importance of precipitation inputs to the material budgets of a lake in our study area.

2. Description of Study Area

Precipitation collectors were located on or near our study lakes in the Haliburton–Muskoka area of central Ontario (Figure 1). This area is underlain by Precambrian bedrock composed primarily of granite gneiss, pegmatite and migmatite. The overburden is glacially derived, usually a shallow till with frequent exposures of bedrock. The area is forested with a mixed deciduous/coniferous forest and no large urban or industrial centers exist within 200 km.

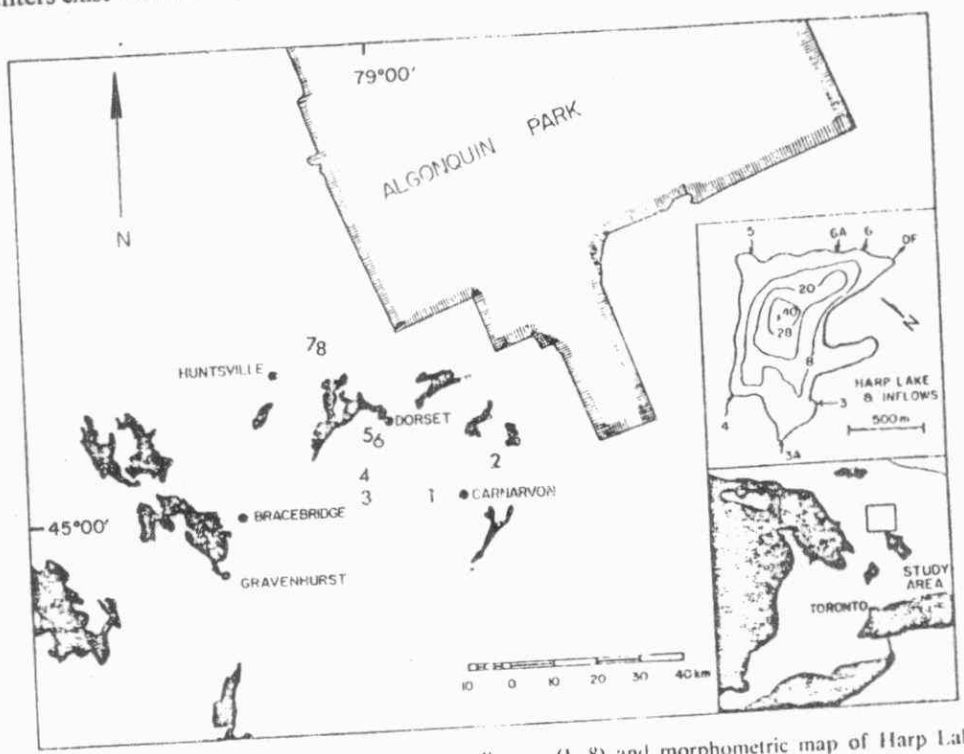


Fig. 1. Study area, location of precipitation collectors (1–8) and morphometric map of Harp Lake, showing location of streams. Collector numbers correspond to those in Figure 2.

Harp Lake (location 8 on Figure 1) is a dilute (mean 1977 conductivity of 35 μmho cm^{-1}), oligotrophic (mean 1977 [P] = 7.6 μg l^{-1}) lake with surface area of 66.9 ha and total drainage basin area (including the lake) of 530 ha. The watershed is underlain by Precambrian granitic gneiss and metasedimentary bedrock. Basal tills cover the high areas of the basin and sand deposits (commonly covered with peat) occur in the valleys. The basin is forested with hemlock and balsam fir in the low-lying areas and maple and birch in the dry upland areas. The 90 dwellings around Harp Lake (Ontario Ministry of Housing, 1977) are used primarily as cottages.

3. Methods

The types of precipitation collected at each site and periods of collector operation are summarized in Figure 2. Battery operated, moisture-activated samplers (Applied Earth Science Consultants) opened automatically during periods of precipitation and collected the 'wet' fraction of precipitation. Samples were removed from the collectors when there was sufficient volume for chemical analysis. Collection periods ranged from 1 to 40 days (winter), most samples being collected weekly. One event sampler (Dorset) was heated for winter use by means of an electric light bulb controlled by a thermostat. Event snow samples were thus melted and kept in the liquid state.

In 1978, bulk rain samples were collected with 0.25 m^2 square, Teflon coated, stainless steel funnels leading into glass bottles. In previous years, smaller polyethylene funnels had been used. Funnels were fitted with 500 μm Nitex mesh to prevent contamination by insects. Samples were visually inspected and any that were obviously contaminated were discarded.

Bulk snow samples were obtained with 63-cm-high, 43-cm-diameter polyethylene containers. Collection periods for bulk precipitation ranged from one to 83 days (winter), most samples being collected weekly or bimonthly. All precipitation collectors

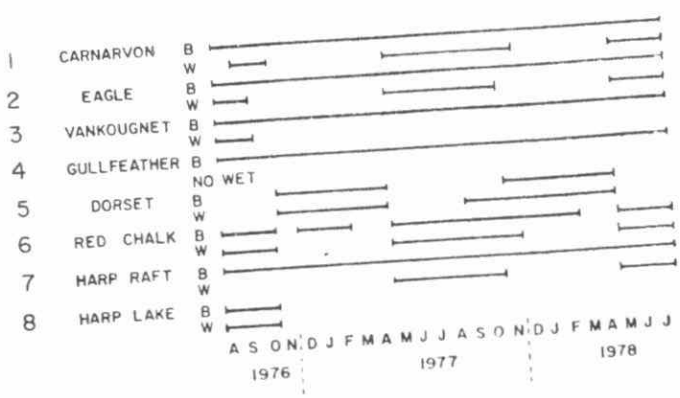

1 CARNARVON B W
2 EAGLE B W
3 VANKOUGNET B W
4 GULLFEATHER B
NO WET
5 DORSET B W
6 RED CHALK B W
7 HARP RAFT B W
8 HARP LAKE B W
A S O N D J F M A M J J A S O N D J F M A M J J
1976
1977
1978

Fig. 2. Period of operation of bulk (B) and wet (W) collectors. Collector numbers correspond to locations on Figure 1.

were about 1 m above ground (or snow) level. Rainfall depth was measured at each collector site using a 10-cm-diameter, polycarbonate rain gauge. Snow samples were melted and their volumes measured to obtain water equivalent depths of snowfall.

Samples were analyzed for total P, total Kjeldahl N, NO_3^-, NH_4^+ and pH at a field laboratory in Dorset within one day of collection. Analyses of Ca^{++}, Mg^{++}, Na^+, K^+, sulphate, chloride and Fe were performed in Toronto within 1 week of collection. All analytical methods except total P (Jeffries *et al.*, 1979) are described in Ontario Ministry of Environment (1975). Total N was calculated as the sum of TKN and NO_3^- since levels of nitrite in the precipitation were negligible.

In our study area, Jeffries *et al.* (1978) have used ANOVA (Analysis of Variance) techniques to show that precipitation loading varied significantly ($\alpha = 0.05$) between rainfall events but not between sites. Therefore, in the calculation of deposition rates it was important to have a complete record of deposition through time. However, each of our collectors missed certain precipitation events due to sampler malfunction, sample breakage, contamination or analytical error. To obtain a complete record of deposition through time, data from the 8 bulk collectors were pooled, as were the data from the 7 'wet' collectors. To pool the data, daily deposition rates (total deposition per collection period/number of days in the period) were calculated for each collector. An arithmetic mean daily deposition was obtained for each day by averaging the daily deposition rates. The mean daily deposition rates were then summed to give monthly and annual deposition figures.

Construction of major ion and nutrient budgets for Harp Lake for January to December 1977 was done using the method described by Scheider *et al.* (1979) for the construction of a total P budget. Hydrological gauging stations, each consisting of a 90° V-notch weir and/or a flume and a Leopold and Stevens Type 71A continuous stage recorder, were constructed on all major streams near their points of entry to Harp Lake. The stream stage records were calibrated to discharge measurements taken 12 to 30 times per year on each stream by the area-velocity method or by catchment. For the area velocity method, the water velocity was measured using a Teledyne Gurley Pygmy Model 625 current meter or an Ott type C31-00 current meter across a surveyed section of stream. The catchment method requires collection of the entire flow of the stream (as it passes over the 90° V-notch weir) in a bucket for a measured time period.

Samples of stream water were taken 27 to 43 times per year from each stream. The water was filtered through a 500 μm mesh net and analyzed in Dorset or Toronto by the methods previously outlined.

4. Results and Discussion

Temporal variations in precipitation composition and deposition are to be expected and inputs to watersheds are best determined from several years data. Schindler *et al.* (1976) have shown that annual bulk depositions of major ions and nutrients varied up to two-fold over a 4 yr period at Rawson Lake northwestern Ontario. Likens *et al.* (1977) found

2 to 8-fold annual variations in Ca^{++}, Mg^{++}, Na^{+}, K^{+}, H^{+}, $SO_4^{=}$, and Cl^{-} depositions over a 7 to 11 yr period at Hubbard Brook, New Hampshire. In this sense, our findings are of a preliminary nature.

Consideration of the depth of precipitation in the study period is important because ionic depositions have been found to vary with the amount of precipitation (Pearson and Fisher, 1971; Likens *et al.*, 1977). The long term, mean annual precipitation depth of the Atmospheric Environment Canada meteorological station closest to our network (Muskoka A, 45 km distant) is 99.3 cm. This is somewhat greater than the 83.2 cm which fell at this station in the period August 1976 to July 1977 but similar to the 94.5 cm measured from August 1977 to July 1978. The mean annual depths of precipitation which fell into our collections vessels were 68.9 cm and 82.7 cm in August 1976 to July 1977 and August 1977 to July 1978, respectively (Figure 3). The discrepancy in the amount of precipitation caught by our collectors and that caught by the closest meteorological station is partially due to natural spatial variability. Differences of up to threefold occurred in the total monthly depth of precipitation measured at the three meteorological stations (Muskoka A, Haliburton, Huntsville) closest to our study area. In the winter months, our snow collectors consistently undercaught the Nipher snow gauge used at the Muskoka A meteorological station. Galloway and Likens (1976) have observed that bulk snow collectors similar to our design have low catch efficiencies. Larson and Peck (1974) summarized several studies showing that shielded gauges (such as the Nipher gauge) have greater catch efficiencies than unshielded gauges because they reduce the effects of wind turbulence around the gauge orifice. Harris and Carder (1974) demonstrated that the Nipher snow gauge had the greatest catch efficiency of several gauges tested. Therefore, it is likely that our deposition rates are underestimates during the winter months.

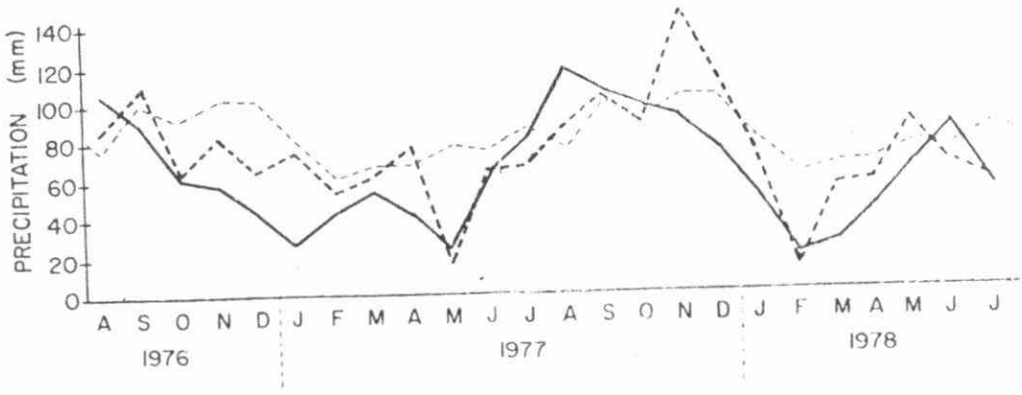


Fig. 3. Long term mean monthly depth of precipitation (mm) at Muskoka A, the Atmospheric Environment meteorological station closest to our network (– · – · – line). Monthly depth of precipitation (mm) measured during the study period at Muskoka A (– – – line) and by gauges used in our network (— — line).

4.1. CONCENTRATION OF IONS IN PRECIPITATION

The volume-weighted, mean annual concentrations of major ions and nutrients in precipitation are summarized in Table I. In the calculation of the mean values, 70 to 194 bulk samples and 51 to 107 samples of wet precipitation were included depending upon the parameter. Annual variation in the mean annual concentrations in the two years of study was as great as twofold in bulk precipitation and almost threefold in wet precipitation. The range in concentrations between individual precipitation samples was 1 to 3 orders of magnitude for both bulk and wet samples, with the greatest range occurring for total P, NH_4^+, and NO_3^-, TKN, total N and H^+.

We were unable to measure a charge balance for either bulk or wet precipitation using the mean annual concentrations (Table II).

Further analysis of the data showed that we failed to measure a charge balance to within 10% on 90% of the individual precipitation samples. Employing the same

TABLE I

Number of analyses (n), range and volume weighted mean annual concentration of major ions and nutrients in bulk and wet precipitation collected in Haliburton-Muskoka. Data are for the periods August 1976–July 1977 and August 1977–July 1978 inclusive. All concentrations are in mg l^{-1}, except pH, with meq l^{-1} in parentheses.

	1976–1977			1977–1978		
	mean	range	n	mean	range	n
bulk total P	0.060	0.005 – 0.720	133	0.035	0.003 – 0.608	173
wet total P	0.024	< 0.0005 – 0.370	74	0.019	0.001 – 0.156	107
bulk NO_3^--N	0.504 (0.036)	< 0.005 – 1.50	87	0.573 (0.041)	< 0.050 – 2.60	140
wet NO_3^--N	0.419 (0.030)	0.035 – 1.80	62	0.448 (0.032)	0.050 – 1.25	76
bulk NH_4^+-N	0.506 (0.036)	0.018 – 1.44	88	0.471 (0.034)	0.005 – 2.80	135
wet NH_4^+-N	0.438 (0.031)	0.043 – 2.37	62	0.342 (0.025)	0.030 – 1.65	73
bulk TKN	0.969	0.050 – 8.23	108	0.738	0.035 – 3.92	167
wet TKN	0.733	0.015 – 2.46	66	0.577	0.065 – 3.15	99
bulk total N	1.473	–	–	1.311	–	–
wet total N	1.152	–	–	1.027	–	–
bulk Fe	0.214	0.03 – 1.90	72	0.103	< 0.01 – 0.85	165
wet Fe	0.171	0.01 – 0.22	52	0.061	< 0.01 – 0.70	96
bulk H^+	4.10 (0.079)	3.22 – 6.88	125	4.15 (0.070)	3.61 – 6.35	194
wet H^+	4.00 (0.100)	2.97 – 6.09	78	4.20 (0.061)	3.45 – 5.99	100
bulk Ca^{++}	0.98 (0.049)	< 0.20 – 3.00	72	0.70 (0.035)	< 0.20 – 2.95	168
wet Ca^{++}	0.71 (0.036)	0.50 – 2.35	52	0.66 (0.033)	< 0.20 – 3.00	97
bulk Mg^{++}	0.15 (0.012)	< 0.05 – 0.60	71	0.10 (0.008)	< 0.05 – 0.46	164
wet Mg^{++}	0.12 (0.010)	< 0.05 – 0.35	51	0.08 (0.007)	0.01 – 0.35	93
bulk Na^+	0.58 (0.025)	0.05 – 2.06	70	0.48 (0.021)	< 0.10 – 4.0	167
wet Na^+	0.39 (0.017)	0.10 – 3.30	52	0.50 (0.022)	< 0.10 – 2.6	99
bulk K^+	0.23 (0.006)	< 0.05 – 2.75	72	0.14 (0.004)	< 0.05 – 0.93	165
wet K^+	0.14 (0.004)	0.05 – 1.25	51	0.09 (0.002)	< 0.05 – 0.61	97
bulk $SO_4^=$	4.3 (0.089)	0.5 – 12.0	83	3.7 (0.077)	1.0 – 15.5	165
wet $SO_4^=$	3.2 (0.067)	0.5 – 11.5	60	3.4 (0.071)	0.5 – 12.1	97
bulk Cl^-	0.46 (0.013)	0.1 – 4.9	85	0.28 (0.008)	0.02 – 0.8	161
wet Cl^-	0.33 (0.009)	0.1 – 2.9	61	0.20 (0.006)	0.09 – 0.6	98

TABLE II

Charge balance for precipitation collected in Haliburton-Muskoka (using mean annual concentrations), Harp Lake water (mean annual concentration) and precipitation collected at other locations on the Precambrian Shield

Site	Sample		Σcations (meq l^{-1})	Σanions (meq l^{-1})	Reference
Haliburton-Muskoka	bulk precipitation	1976 – 1977	0.208	0.138	this study
Haliburton-Muskoka	wet precipitation	1976 – 1977	0.198	0.106	this study
Haliburton-Muskoka	bulk precipitation	1977 – 1978	0.171	0.126	this study
Haliburton-Muskoka	wet precipitation	1977 – 1978	0.150	0.109	this study
Haliburton-Muskoka	Harp Lake water	1977	0.297	0.333	this study
N.W. Ontario	bulk precipitation	1970 – 1973	0.074	0.119	Schindler *et al.* (1976)
Killarney Mts. Ont.	bulk precipitation	1972	0.098	0.135	[a]Beamish and Van Loon (1977)
Killarney Mts. Ont.	bulk precipitation	1973	0.085	0.114	[a]Beamish and Van Loon (1977)

[a]No measured values for NH_4^+ or NO_3^-.

analytical methods, a charge balance of within 10% was achieved for Harp Lake water using the mean concentrations for 1977. However, concentrations of major ions in precipitation are lower (except H^+) than lakewater concentrations and are, in fact, near the lower end of the analytical range. The imprecision of the analytical methods at the low concentrations could be a factor in explaining the lack of charge balance. However, the systematic excess of positive charge in the individual precipitation samples suggests the presence of unmeasured anions rather than random analytical errors. Although we did not attempt to measure bicarbonate or organic acids in the precipitation, their contribution to the charge balance would be small at the low pH normally found in precipitation in our study area. Concentrations of F^- were 2 to 5 μeq l^{-1} in precipitation, but the small number of analyses performed precluded inclusion of F^- in the charge balance calculation. Negatively changed Mn oxides, Fe oxides and silicates found in soil particulates may be of greater significance. These particulates can be washed out and be included in the wet component of precipitation or settle out by gravity for inclusion in the dry deposition.

Others working on precipitation in areas underlain by the Canadian Shield also did not measure a charge balance (Table II). Schindler *et al.* (1976) and Beamish and Van Loon (1977) measured an excess of anions. Although Beamish and Van Loon (1977) did not analyze their precipitation for NH_4^+ or NO_3^-, these ions approximately balance in precipitation.

The ionic composition of bulk and wet precipitation was such that on an equivalent basis $SO_4^= > NO_3^- > Cl^-$ for the anions and $H^+ > Ca^{++} > NH_4^+ > Na^+ > Mg^{++} > K^+$ for the the cations in both years studied. Others (Schindler *et al.*, 1976; Kramer, 1976; Swanson, 1976; Beamish and Van Loon, 1977) collecting precipitation in areas underlain by the Canadian Shield also report the same order of anion dominance, as do Likens *et al.*

(1977) in New Hampshire. However, whereas our results and those of Beamish and Van Loon (1977) found H^+ to be the dominant cation, Schindler *et al.* (1976) and Kramer (1976) reported Ca^{++} and Mg^{++} respectively to be most abundant. Kramer's high Mg^{++} values can be partially accounted for by the fact that part of his network was situated in areas underlain by carbonate bedrock.

The dominant anion on an equivalent basis in precipitation in our study area is $SO_4^=$, with H^+ the dominant cation. Although this suggests that H_2SO_4 is responsible for the low pH in precipitation, we have not attempted to proportion the acidity between different chemical species. Previous studies (Dillon *et al.*, 1978) have shown that 46 to 71% of the total acidity (defined as the amount of NaOH required to raise sample pH to 9.00) measured in 4 precipitation events collected by our network is accounted for by free acidity (free acidity = 10^{-pH}). These results are similar to those of Galloway *et al.* (1976) at Ithaca, N.Y., Hubbard Brook and Adirondack Mountains, N.Y. who reported that 50 to 83%, 89 to 102% and 80 to 89% respectively of the total acidity was in the free state.

As previously reported by Dillon *et al.* (1978), precipitation in Haliburton-Muskoka is as acidic or more acidic than that falling in Sudbury, Ontario, southern Scandinavia or the northeastern U.S.A. areas where the acidification of freshwaters has been documented (Conroy *et al.*, 1975; Gjessing *et al.*, 1976; Schofield, 1976). Preliminary surveys indicate that lakes and rivers in Haliburton-Muskoka are also being affected (Dillon *et al.*, 1978; Scheider *et al.*, 1978). Low pH has been shown to detrimentally affect communities of phytoplankton (Yan, 1979; Kwiatkowski and Roff, 1976), zooplankton (Sprules, 1975), macrophytes (Gorham and Gordon, 1963) and fish (Beamish and Harvey, 1972; Beamish, 1974,1976; Beamish *et al.*, 1975) in Ontario.

There are several possible sources of the acidic materials falling in precipitation. Major ore smelting centres are located to the north and northwest of Haliburton-Muskoka and large urban/industrial centers in Canada and the U.S.A. exist to the south and southwest. Studies by Millan and Chung (1977), Lafleur and Whelpdale (1977) and Chung (1978) have shown that long range transport is such that both source areas can impact on Haliburton-Muskoka. Air trajectory analyses are presently being conducted on our precipitation data to determine sources of acidity.

4.2. PRECIPITATION DEPOSITION RATES

Annual deposition rates for Haliburton-Muskoka are summarized in Table III and compared to values reported by others working in areas underlain by the Canadian Shield. A complete review of precipitation loading rates to forested watersheds in several different areas of the world is given by Likens *et al.* (1977). In most cases, our bulk deposition rates fell within the range of reported literature values. Two notable exceptions were H^+ and $SO_4^=$. Deposition of these ions in our study area was higher than at any other location on the Canadian Shield. Our H^+ depositions fell at the high end of the range (6.6 to 67 meq m^{-2} yr^{-1}) reported by Pearson and Fisher (1971) for 18 sites in the northeastern U.S.A., but were somewhat lower than the values (76 to 118 meq m^{-2} yr^{-1})

TABLE III

Annual deposition of major ions and nutrients in bulk (B) and wet (W) precipitation in Haliburton-Muskoka for periods August 1976 – July 1977 and August 1977 – July 1978. Results of other studies done in areas of Ontario underlain by the Precambrian Shield are included. Units are in mg m^{-2} yr^{-1} with at $^{-2}$ yr^{-1} in brackets.

Substance	Type	Annual deposition 1976 – 1977	1977 – 1978	Annual bulk deposition reported in other studies[a]	
Total P	B	41.5	28.9	Swanson (1976)	5.6
	W	16.7	15.6	Foster (1974)	9.0
				Kramer (1976)	20.1
				Schindler *et al.* (1976)	32.5
				Scheider (1978)	35.0
				Schindler and Nighswander (1970)	35.0
				Gomolka (1975)	36.9
				Cross (1977)	41.3
				Nicholls and Cox (1978)	74.4
				Dillon (1974)	77.2
NO_3^--N	B	347 (24.8)	473 (33.8)	Kramer (1976)	281 (20.1)
	W	289 (20.6)	370 (26.4)		
NH_4^+-N	B	348 (24.9)	389 (27.8)		
	W	301 (21.5)	283 (20.2)		
TKN	B	667	611	Kramer (1976)	372
	W	505	478		
				Foster (1974)	495
Total N	B	1015	1084	Schindler *et al.* (1976)	625
	W	794	849	Kramer (1976)	653
				Swanson (1976)	680
				Nicholls and Cox (1978)	1600
Fe	B	147	84.8	Schindler *et al.* (1976)	negligible
	W	118	50.6	Swanson (1976)	118
				Kramer (1976)	138
				Cross (1977)	454
H^+	B	(54.6)	(58.2)	Schindler *et al.* (1976)	(10)
	W	(69.1)	(50.7)	Kramer (1976)	(11.6)
				Beamish and Van Loon (1977)	(33.3)
				Beamish and Van Loon (1977)	(55.9)
Ca^{++}	B	676 (33.8)	578 (28.9)	Schindler *et al.* (1976)	379 (18.9)
	W	492 (24.6)	548 (27.4)	Swanson (1976)	401 (20)
				Kramer (1976)	950 (47.4)
				Foster (1974)	1118 (55.8)
				Schindler and Nighswander (1970)	1412 (70.5)
Mg^{++}	B	102 (8.37)	80.9 (6.66)	Swanson (1976)	68.1 (5.6)
	W	85.9 (7.07)	67.1 (5.52)	Foster (1974)	83.9 (6.9)
				Schindler *et al.* (1976)	92.4 (7.6)
				Schindler and Nighswander (1970)	540 (44.4)
				Kramer (1976)	876 (72.1)
Na^+	B	402 (17.5)	393 (17.1)	Schindler and Nighswander (1970)	127 (5.5)
	W	269 (11.7)	414 (18.0)	Schindler *et al.* (1976)	159 (6.9)
				Swanson (1976)	182 (7.9)
				Kramer (1976)	1048 (45.6)
K^+	B	159 (4.06)	114 (2.91)	Schindler and Nighswander (1970)	94 (2.4)
	W	96.6 (2.47)	74.7 (1.91)	Schindler *et al.* (1976)	109 (2.8)
				Swanson (1976)	156 (4.0)
				Kramer (1976)	211 (5.4)
				Foster (1974)	809 (20.7)
$SO_4^=$	B	2960 (61.6)	3080 (64.1)	Schindler *et al.* (1976)	944 (20.7)
	W	2210 (46.0)	2810 (58.5)	Kramer (1976)	2600 (54.1)
				Swanson (1976)	2670 (55.6)
Cl^-	B	314 (8.85)	229 (6.46)	Schindler *et al.* (1976)	266 (7.5)
	W	226 (6.38)	167 (4.71)	Kramer (1976)	269 (7.6)
				Swanson (1976)	666 (18.8)

[a] Deposition reported by Schindler and Nighswander (1970) is mostly wet, but includes some dry deposition.

measured by Likens *et al.* (1977) for Hubbard Brook. The annual deposition of H^+ in wet precipitation is similar to values reported for Norway (54 to 90 meq m^{-2} yr^{-1}) by Gjessing *et al.* (1976).

Annual wet deposition averaged 47% of bulk deposition for total P in the 2 yr study period. Wet deposition was >60% of bulk deposition for the other ions (mean wet/bulk = 80%, range 64% for K^+ to 107% for H^+). Gomolka (1975) and Nicholls and Cox (1978) observed by microscopic examination that dust, pollen and plant debris comprised the particulates in bulk precipitation samples collected on rafts in lakes near our study area. The composition of the aerosol and gaseous fraction of the bulk input is unknown. Although difficult to measure and generally smaller than the wet fraction of precipitation, dry deposition (especially of P) should be taken into account when calculating the precipitation input to lakes. Bulk precipitation is an easily measured approximation of the total input to a lake by precipitation.

In 1976–1977, the wet deposition of H^+ was greater than the bulk deposition, whereas in 1977–1978 the reverse was true. This observation points to the variability of the deposition figures. Several factors may account for the difference in deposition in the 2 yr. Particulate material of a calcareous nature may act to buffer the precipitation pH (Winkler, 1976; Dillon *et al.*, 1978). The existence of acidic aerosols may be implied or the different collectors employed may have different catch efficiencies.

Seasonal patterns in bulk and wet deposition with maxima occurring in the summer were noted for total P, TKN, total N, Ca^{++}, Mg^{++}, Na^+, K^+, and $SO_4^=$ (Figure 4). Nitrate, Fe, H^+ and Cl^- showed no clear seasonal trends in deposition. These patterns are in part due to a similar seasonal trend in precipitation depth. Additionally, those ions showing summer maxima in deposition were generally present in higher concentrations in the summer months. The fact that wet depositions exhibited summer maxima indicates that factors other than an increase in particulate deposition were causing the trend. Seasonal differences in air mass origins and the associated differences in precipitation chemistry may be a factor.

In the Haliburton-Muskoka area, precipitation falling on the lake surface from approximately December to March inclusive remains on the ice until spring thaw, (excepting some drifting and exchange with lake water through cracks in the ice). With respect to the lake, precipitation falling during this period can be treated as a single input. Depending upon the parameter, deposition in this period represented 8 to 38% of the annual deposition of bulk precipitation in the two years of study. The fraction of the annual deposition that fell during the winter months was lowest for total phosphorus in both years. Viewed in this way, the input of ions and nutrients to the lake by precipitation was generally greatest in the spring.

4.3. IMPORTANCE OF PRECIPITATION TO SUBSTANCE BUDGETS OF HARP LAKE

A majority of the few measured substance budgets of lakes has been done for total P because of its importance as an algal nutrient. Only Schindler *et al.* (1976) give measured major ion budgets for a lake on the Canadian Shield. Henriksen and Wright (1976) have

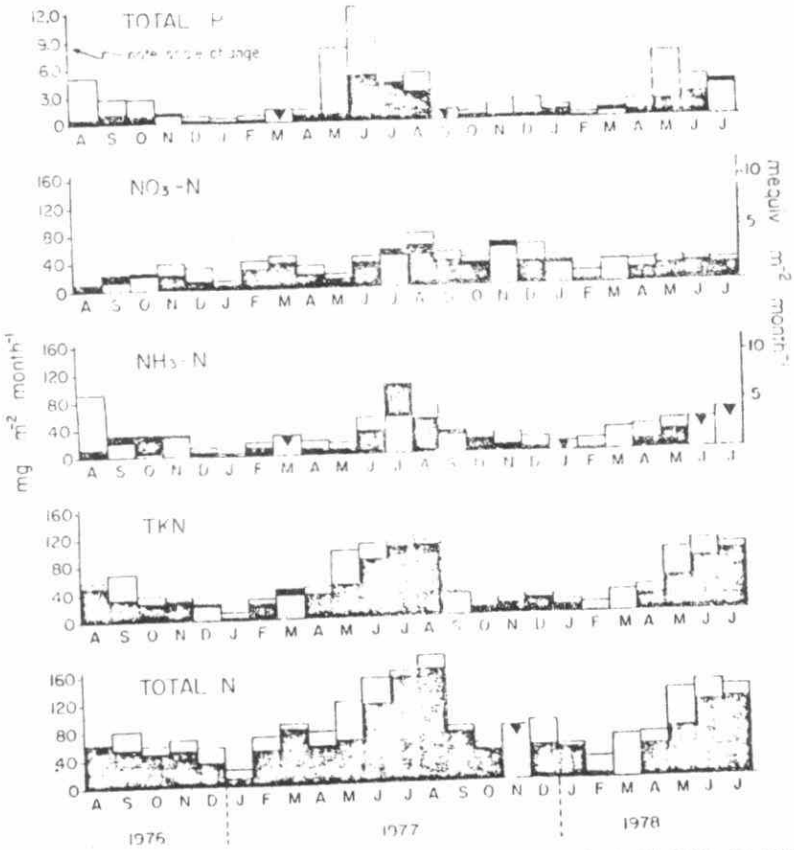


Fig. 4. Mean monthly deposition of (a) total P, (b) NO_3^--N, (c) NH_4^+-N, (d) TKN, (e) total N, (f) H^+, (g) Ca^{++}, (h) Na^+, (i) Mg^{++}, (j) K^+, (k) SO_4, (l) Cl^-, and (m) Fe in mg m^{-2} month $^{-1}$ and meq m^{-2} month $^{-1}$.

bulk deposition
wet deposition

wet deposition
bulk deposition

bulk equals wet deposition
desposition negligible

measured the major ion budgets for a small, acidic lake underlain by granitic bedrock in S. Norway. A complete presentation and discussion of the hydraulic and substance budgets of Harp Lake and the other lakes in our study will be given in a later paper. In Table IV, we give precipitation input as a percent of the total input to Harp Lake for the period January–December 1977, excluding any input from the 90 dwellings on the shore of the lake. Comparative values from the literature are also included.

The surface of Harp Lake represents 12.6% of the total watershed area. Consequently, precipitation input directly to the lake would be 12.6% of the total input if the terrestrial watershed did not retain or contribute material to the lake. Precipitation on the lake surface contributed >12.6% of the total input of water (20%), H^+ (82%), total P (44%), NO_3^--N (67%), NH_4^+-N (73%), TKN (35%) and total N (44%), indicating that the terrestrial portion of the watershed retains these substances. The net terrestrial

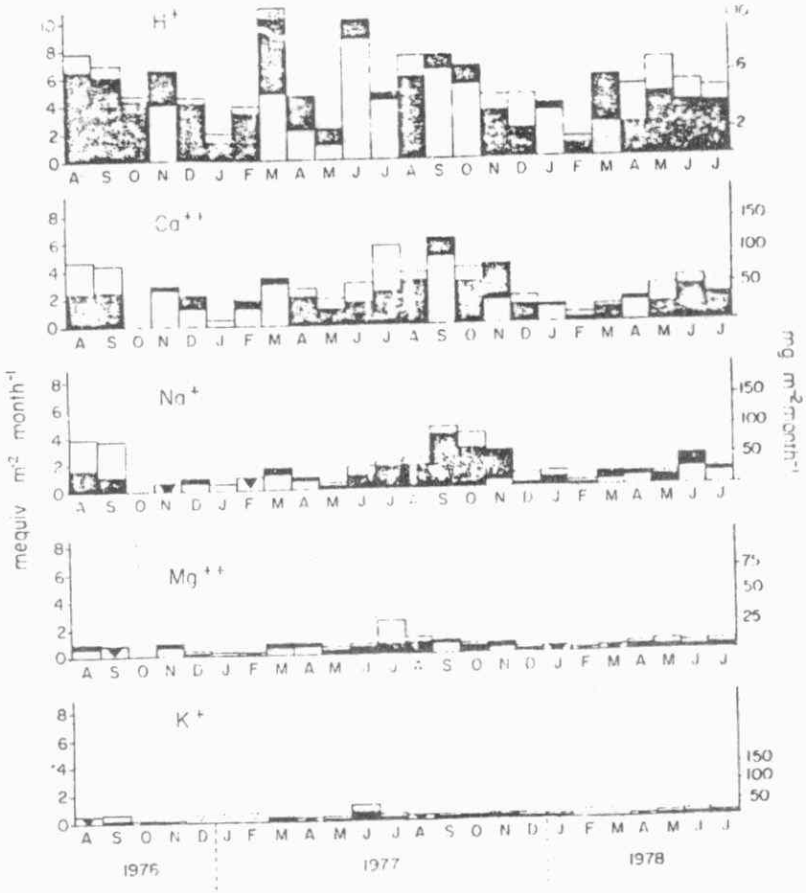


Fig. 4. Mean monthly deposition of (a) total P, (b) NO_3^--N, (c) NH_4^+-N, (d) TKN, (e) total N, (f) H^+, (g) Ca^{++}, (h) Na^+, (i) Mg^{++}, (j) K^+, (k) $SO_4^=$, (l) Cl^-, and (m) Fe in mg m^{-2} $month^{-1}$ and meq m^{-2} $month^{-1}$.

bulk deposition
wet deposition

wet deposition
bulk deposition

bulk equals wet deposition
deposition negligible

retention of water, total P, and the N compounds is probably due to biological uptake by the flora, whereas H^+ retention is likely related to weathering reactions. For the remaining ions, precipitation contributed 3 to 11% of the total input to the lake, indicating that these ions are weathered from the watershed.

Schindler *et al.* (1976) reported that the precipitation input to the surface of Rawson Lake (lake area = 13.7% of drainage basin area) contributed >13.7% of the total input of total P, total N, H^+, water and Cl^- and less than 13.7% of the total input of Fe, Ca^{++}, Mg^{++}, Na^+, K^+, and $SO_4^=$. Henriksen and Wright (1976) assumed a Cl^- balance for Langtjern in S. Norway (lake area = 4.8% of drainage basin area) and reported that the direct precipitation input to Langtjern was > 4.8% of the total input for H^+ and NO_3^-

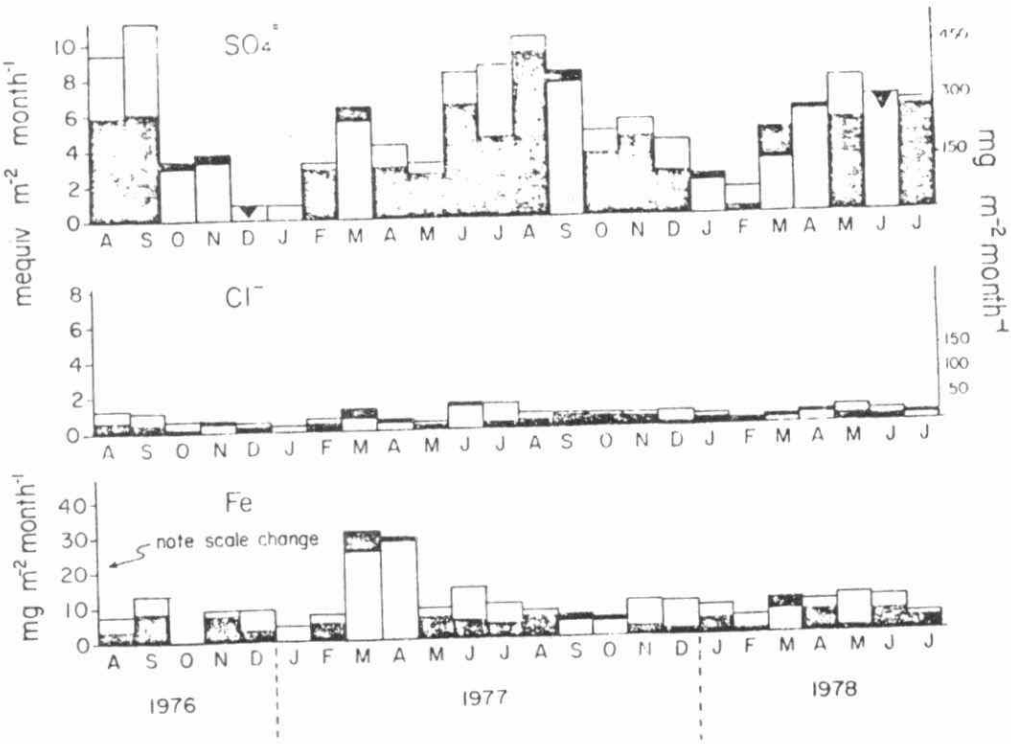


Fig. 4. Mean monthly deposition of (a) total P, (b) NO_3^--N, (c) NH_4^+-N, (d) TKN, (e) total N, (f) H^+, (g) Ca^{++}, (h) Na^+, (i) Mg^{++}, (j) K^+, (k) $SO_4^=$, (l) Cl^-, and (m) Fe in mg m^{-2} $month^{-1}$ and meq m^{-2} $month^{-1}$

bulk deposition
wet deposition

wet deposition
bulk deposition

bulk equals wet deposition
deposition negligible

and $\leq 4.8\%$ of the total input for Ca^{++}, Mg^{++}, Na^+, K^+, and $SO_4^=$. Likens *et al.* (1977) have summarized several studies on the substance budgets of terrestrial watersheds and found that Ca^{++}, Mg^{++}, Na^+, and K^+ are lost from the watershed, P and N are generally retained by the watershed and $SO_4^=$ may be either lost or retained. These results agree with our findings and show that the precipitation input directly to the surface of a lake is especially important in the construction of the hydraulic, total P, N, and H^+ budgets of the lake. Alternately stated, the terrestrial watershed retains these substances; hence, precipitation input directly on the lake is of greater relative significance.

5. Summary

In summary, the chemistry of the precipitation in Haliburton-Muskoka is dominated by H^+ and $SO_4^=$ ions, and the deposition of these ions is higher in Haliburton-Muskoka than at any other location on the Canadian Shield measured to date. Wet deposition

TABLE IV

Input of major ions and nutrients in bulk precipitation as a percentage of the total input to Harp Lake for the period of January–December 1977. Results of others working in areas underlain by similar bedrock are included.

Substance	This study	Schindler *et al.* (1976)	Henriksen and Wright (1976)	Other studies	
total P	44	46 – 55%	–	0.3 – 79	Dillon (1974)
				4 – 40	Scheider (1978)
				23	Cross (1977)
NO_3^--N	67	–	67	–	
NH_4^+-N	73	–	–	–	
TKN	35	–	–	–	
total N	44	45 – 54	–	–	
Fe	11	negligible	–	11	Cross
H^+	82	43 – 50	12	–	
Ca^{++}	5	3 – 8	1.2	–	
Mg^{++}	3	4.9 – 6.4	1.4	–	
Na^+	11	4.5 – 7.4	4.2	–	
K^+	9	1.2 – 9.7	4.3	–	
$SO_4^=$	7	13	4.8	–	
Cl^-	9	26 – 42	4.7	–	
H_2O	20	26 – 34	–	–	

generally contributes the greatest fraction of the precipitation input to a lake. Seasonal patterns in bulk and wet deposition with summer maxima are found for most substances with the exception of H^+, NO_3^-, Cl^-, and Fe, which show no distinct trends. The watershed of Harp Lake retained P, N, H^+, and water and consequently the precipitation input directly to the lake surface was of greater relative importance for these materials.

Acknowledgments

We thank R. Reid and J. Moss for assistance with sample collection. C. Chun and N. Nicolls performed the chemical analyses in Dorset. P. J. Dillon and D. S. Jeffries provided valuable ideas and discussion. Drs. F. Elder, D. Whelpdale, and L. Shenfield critically commented on the manuscript. This study was funded by the Lakeshore Capacity Study.

References

Beamish, R. J.: 1974, *Wat. Res.* **8**, 85.
Beamish, R. J.: 1976, *Water, Air, Soil Pollut.* **6**, 501.
Beamish, R. J. and Harvey, H. H.: 1972, *J. Fish. Res. Bd. Canada* **29**, 1131.
Beamish, R. J. and Van Loon, J. C. L.: 1977, *J. Fish. Res. Bd. Canada* **34**, 649.
Beamish, R. J., Lockhart, W. L., Van Loon, J. C., and Harvey, H. H.: 1975, *Ambio* **4**, 98.
Chung, V. S.: 1978, *Atmos. Environment* **12**, 1471.

Conroy, N., Hawley, K., Keller, W., and Lafrance, C.: 1975, 'Influences of the Atmosphere on Lakes in the Sudbury area', in: Proc. First Specialty Symp. on *Atmospheric Contribution to the Chemistry of Lake Waters*. Internat. Assoc. Great Lakes Res., 20 September–1 October 1975, 146.
Cross, P. M.: 1977, 'An attempt to estimate phosphorus retention in Bob Lake from iron retention and the iron: phosphorus ratio in the sediments'. M.Sc. Thesis, University of Toronto, 121 pp.
Dillon, P. J.: 1974, 'The prediction of phosphorus and chlorophyll concentrations in lakes'. Ph.D. Thesis, University of Toronto, 330 pp.
Dillon, P. J., Jeffries, D. S., Snyder, W., Reid, R., Yan, N. D., Evans, D., Moss, J., and Scheider, W. A.: 1978 1979, *J. Fish. Res. Bd. Canada* **35**, 809.
Foster, N. W.: 1974, *Can. J. Forest Res.* **4**, 470.
Galloway Galloway, J. N. and Likens, G. E.: 1976, *Water, Air, Soil Pollut.* **6**, 241.
Galloway, J. N. and Likens, G. E.: 1978, *Tellus* **30**, 71.
Galloway, J. N., Likens, G. E., and Edgerton, E. S.: 1976, *Water, Air, Soil Pollut.* **6**, 435.
Gjessing, E. T., Henriksen, A., Johannessen, M., and Wright, R. F.: 1976, 'Effects of acid precipitation on freshwater chemistry'. p. 65 in: *Impact of Acid Precipitation on Forest and Freshwater Ecosystems in Norway*. (Braekke, F. H. ed.) SNSF rep. No. 6, SNSF – project 1432 Aas – NLH, Oslo, Norway. 111 pp.
Gomolka, R. E.: 1975, 'An investigation of atmospheric phosphorus as a source of lake nutrient'. M.Sc. Thesis, University of Toronto, 167 pp.
Gorham, E.: 1951, *Geol. Soc. Amer. Bull.* **72**, 795.
Gorham, E. and Gordon, A. G.: 1963, *Can. J. Bot.* **41**, 371.
Harris, R. E. and Carder, A. C.: 1974, *Can. J. Earth Sci.* **11**, 557.
Henriksen, A. and Wright, R. F.: 1976, 'Effects of acid precipitation on a small acid lake in southern Norway'. *Nordic Hydrology* **8**, 1.
Jeffries, D. S., Snyder, W. R., Scheider, W. A., and Kirby, M.: 1978, 'Small-scale variations in precipitation loading near Dorset, Ontario'. Proc. 13th Canadian Symp. Water Poll. Research Canada p. 73.
Jeffries, D. S., Dieken, F. P., and Jones, D. E.: 1979, *Water Research* **13**, 275.
Kramer, J. R.: 1976, 'Fate of atmospheric sulphur dioxide and related substances as indicated by chemistry of precipitation'. Unpub. report 199 pp.
Kwiatkowski, R. E. and Roff, J. C.: 1976, *Can. J. Bot.* **54**, 2546.
Lafleur, R. J. and Whelpdale, D. M.: 1977, 'Spatial distribution of sulphates over eastern Canada during August 1976'. Presented at 70th Annual Meeting of the Air Pollution Control Assoc., Toronto, Ontario, Canada, June 1977.
Larson, L. W. and Peck, E. L.: 1974, *Water Resour. Res.* **10**, 857.
Likens, G. E., Bormann, F. H., Pierce, R. S., Eaton, J. S. and Johnson, N. M.: 1977, *Biogeochemistry of a forested ecosystem*. Springer-Verlag, New York, 146 pp.
Millán, M. M. and Chung, Y. S.: 1977, *Atmos. Environment* **11**, 939.
Nicholls, K. H. and Cox, C. M.: 1978, *Water Resour. Res.* **14**, 589.
Ontario Ministry of Housing: 1977, personal communication.
Ontario Ministry of the Environment: 1975, 'Outline of analytical methods'. Ont. Min. Environment, 130 pp.
Pearson, F. J. and Fisher, D. W.: 1971, 'Chemical composition of atmospheric precipitation in the North-eastern United States'. United States Geol. Survey Water Supply Paper 1535-P. Washington, D.C. 23 pp.
Scheider, W. A.: 1978, *J. Fish. Res. Bd. Canada* **35**, 300. 1979a, Internat. Assoc. Great Lakes Res. **5**(1), 45
Scheider, W. A., Jeffries, D. S., and Dillon, P. J.: ~~1978, *J. Great Lakes Res.* (in press)~~
Scheider, W. A., Moss, J. J., and Dillon, P. J.: 1979b, 'Measurement and uses of hydraulic and nutrient budgets'. Proc. of a National Conference on Lake Restoration, Minneapolis, Minnesota, U.S.A. August 1978. EPA 440/5–79–001.
Schindler, D. W. and Nighswander, J. E.: 1970, *J. Fish. Res. Bd. Canada* **27**, 2009.
Schindler, D. W., Newburry, R. W., Beatty, K. G., and Campbell, P.: 1976, *J. Fish. Res. Bd. Canada* **33**, 2526.
Schofield, C. L.: 1976, *Ambio* **5**, 228.
Sprules, W. G.: 1975, *J. Fish. Res. Bd. Canada* **32**, 389.
Swanson, D. L.: 1976, 'Atmospheric input of pollutants to the Upper Great Lakes'. Proc. 10th Annual Conference on Trace Substances in Environmental Health. p. 197.
Whitehead, H. C. and Feth, J. H.: 1964, *J. Geophys. Res.* **69**, 3319.
Winkler, E. M.: 1976, *Water, Air, Soil Pollut.* **6**, 295.
Yan, N. D.: 1979, *Water, Air, Soil Pollut.* **11**, 43.

Bulk Precipitation as % Total INPUT To Harp Lake 1977

	%
H	82
NO_3	67
NH_4	73
H_2O	20
Na	11
K	9
Cl	9
SO_4	7
Ca	5
Mg	3

1977 - 1978 [meq l^{-1}]

Bulk

H^+	70	SO_4	77
Ca	35	NO_3	41
NH_4	34	Cl	8
Na	21		126
Mg	8		
K	4		
	171		

Wet

H^+	61	SO_4	71
Ca	33	NO_3	32
NH_4	25	Cl	6
Na	22		109
Mg	7		
K	2		
	150		

APPENDIX TEN

Heavy Metal Deposition - D. Jeffries

Various workers have shown that direct atmospheric deposition of certain metals near centers of anthropogenic activity may constitute a significant portion of the total input into lake ecosystems. There is also evidence that some metals are subject to long range transport since dramatic increases in their concentration in recent Greenland snow samples and the recent sediments of undisturbed lakes have been observed. In view of these observations and as part of two larger studies dealing with the effect of anthropogenic activities on the chemical budgets of some lakes in central Ontario, we have measured the area through collection of bulk and wet-only precipitation samples.

Figure One is a map of the study area. There are four sampling locations as below:

1. Muskoka-Haliburton with 7 samplers.

2. Sudbury North with 4 samplers.

3. Sudbury Center with 2 samplers.

4. Sudbury South with 2 samplers.

Note the lack of sources at the Muskoka-Haliburton station and the major source in the Sudbury area. Also, for the Sudbury stations, please note the distance and direction of these stations from the source. (N.B. Map scale is not entirely accurate.)

...../ii

Stunted and sparse vegetation characterizes the watersheds of our study lakes near the Sudbury Center and Sudbury South precipitation stations, while Sudbury North is not as affected. The vegetation kill may be attributed to the smelting practises used in the early part of the century; however, now most of the smelter emissions, from one of the largest nickel refining operations in the world, are dispersed via the famous 381 m stack although low-level vent fugitive emissions and entrainment from slag and/or tailings piles are still important sources.

The deposition of Pb (at Muskoka-Haliburton station only), Cu, Ni, Zn, Al, Mn, and Fe was measured for a 12 month period at Muskoka-Haliburton and for a 36 month period at the Sudbury stations. Metal deposition for any station was calculated by averaging the measured daily deposition for all the collectors within the station and summing over the desired time period. Large variations in monthly deposition were observed at all stations with the largest variability occurring at the Sudbury stations. Figure Two serves to illustrate this variability for copper deposition. (Please note the different y-axis scales and lack of data points.) Clearly, the degree of variation shown here underlines the need for a long-term sampling program in order to obtain good average values. Still, there is a seasonal pattern of variation for Cu, Ni, and Zn. Cu (see Figure Two) shows summer maxima for Muskoka-Haliburton and Sudbury North and winter maxima for Sudbury Center and Sudbury South due to:

a) the greater availability of entrained dust during the summer, coupled with

b) predominantly south-westerly winds blowing at this time of year.

When there is no snow cover in Muskoka-Haliburton and winds are from the southwest, then Muskoka-Haliburton (local entrainment) and Sudbury North (deposition of stack emissions) receive maximum loading during the summer; conversely, winter maxima occur at Sudbury Center and Sudbury South since the winds predominantly come from the northern gradient thereby dispersing stack emissions towards these stations.

As regards the other metals, Ni shows virtually an identical pattern to Cu and Zn: however, it exhibits summer maxima at all stations suggesting that only entrainment is important for this element. In contrast to Cu, Ni, and Zn, Al (see Figure Three) Fe, Mn, and Pb (for Muskoka-Haliburton station only) show no obvious seasonal patterns though the marked monthly variability is still present. Note that there is only a 2X variation in the y-axis for this major lithologic element (Al) compared to the 100X for Cu.

In Figure Four, the deposition (mg/m/yr) and volume-weighted concentration (µg/L) for Cu and Ni in bulk precipitation at our four stations are shown. For comparison purposes, the median values for rural and urban/industrial North America and Europe (obtained from an extensive literature survey) are illustrated as well. Background concentrations are represented by Greenland and Antarctic snow concentrations (also given in Figure Four).

...../iv

We found that the Cu and Ni values at Muskoka-Haliburton are lower than other rural North American and European values but that the Sudbury data for all three stations exceeded almost all of those values in the literature for urban/industrial environments. Also, Cu and Ni values can be correlated to distance from the source with Sudbury North the lowest and farthest away and Sudbury Center the highest and closest. Therefore, the smelting industry at Sudbury is obviously a massive source for these metals. Even the comparatively uncontaminated Muskoka-Haliburton samples are several times higher in concentration than background values.

Figure Five illustrates Pb and Zn deposition and volume-weighted concentrations. Once again, both Pb and Zn values at Muskoka-Haliburton are lower than the median values for rural North America and Europe, but still an order of magnitude higher than background. For Zn, the Sudbury stations are 3 - 5 times higher than Muskoka-Haliburton and roughly consistent with rural values for North America and Europe (i.e. well below the urban/industrial counterparts.) These results for Zn, plus the lack of correlation of the Sudbury stations with distance from the source suggest that the smelters are not a significant source for this metal.

Al and Fe are major lithologic elements and their redistribution in the environment is expected to predominantly occur by natural processes, and indeed, (see Figure Six) the deposition and concentration of Al are similar at Muskoka-Haliburton and the Sudbury stations in support of this

...../v

expectation. Our Al values are at least two times lower than the median for rural Europe, but an order of magnitude above background levels. On the other hand, higher Fe values close to the Sudbury smelters, Sudbury Center and Sudbury South stations, suggest that this industry is a significant source for Fe, but that the effect is very localized since Sudbury North and Muskoka-Haliburton have virtually identical values which are generally less than rural medians but approximately 20 times higher than background levels.

We also measured metals in wet-only precipitation. In Figure Seven, volume-weighted concentrations are shown. (Note: No data for Sudbury South Station.) The values generally fall at the low end of the range for the wet-only data available in the literature, except the Cu and Ni values at the Sudbury Center station which exceed almost all other reported data. Pb, Cu, and Zn concentrations at Muskoka-Haliburton are similar to those in rural areas of the U.S.

The wet-only fraction constitutes a much higher proportion of the bulk at Muskoka-Haliburton (50 - 82% depending on the metal) compared to Sudbury (13 - 65% depending on the metal). The higher component of particulate dry deposition near to Sudbury is consistent with the hypothesis that most of the metals emitted at Sudbury are deposited within a short distance (< 100 km).

Finally, in Figure Eight, the crustal enrichment factors for Cu, Ni, Pb, Zn, and Fe were calculated assuming that the Al measured in the precipitation samples was of crustal origin. Values approaching

...../vi

one indicate that the element is probably of crustal origin. Therefore, some other source, either natural or anthropogenic, must be involved to explain the higher values. Clearly, all the elements except Fe are enriched relative to Al even at the Muskoka-Haliburton station and the influence of the smelting industry at Sudbury for Cu, Ni, and Fe is clear, while Zn enrichment cannot be easily explained by this activity.

In summary, the following points were recalled:

1) Large variations in monthly deposition of all metals were observed; Cu, Ni, and Zn exhibited seasonal patterns.

2) Comparison of these results with summarized data for Europe and North America showed Muskoka-Haliburton to have generally lower values than the corresponding rural median values, while at Sudbury, Cu, Ni, and Fe deposition is elevated and Zn and Al deposition is not.

3) A strong inverse relationship between Cu, Ni, and Fe deposition with distance from the smelting industry is apparent.

4) The per cent of bulk precipitation supplied by the wet-only fraction is much greater for Muskoka-Haliburton than for the Sudbury stations consistent with the hypothesis that a major portion of the metals emitted by the smelting industry are deposited nearby.

FIGURE ONE

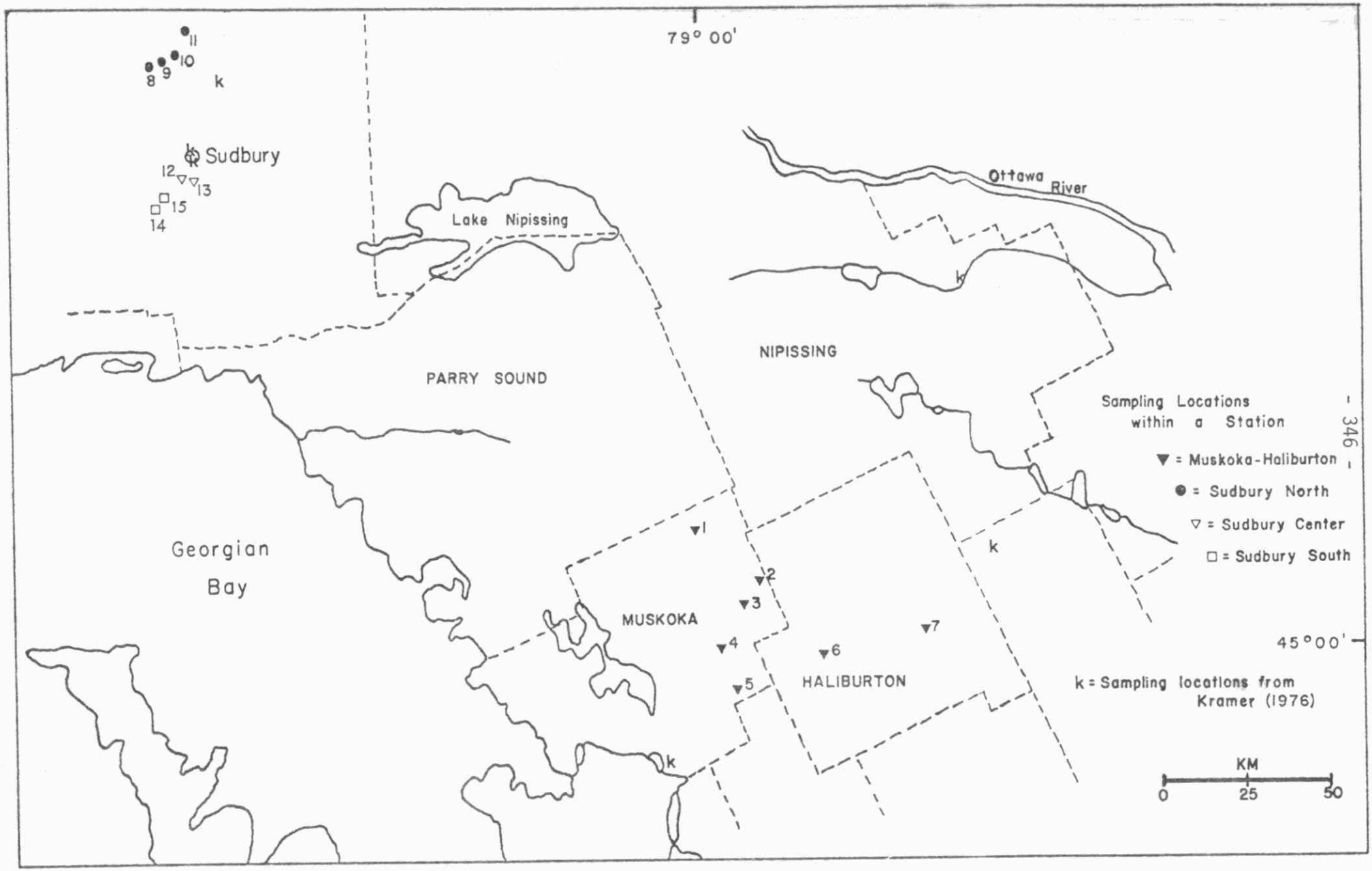

79° 00'
Sudbury
Lake Nipissing
Ottawa River
PARRY SOUND
NIPISSING
Georgian Bay
MUSKOKA
HALIBURTON
45°00'
Sampling Locations within a Station
▼ = Muskoka-Haliburton
● = Sudbury North
▽ = Sudbury Center
□ = Sudbury South
k = Sampling locations from Kramer (1976)
KM
0
25
50
- 346 -

FIGURE TWO

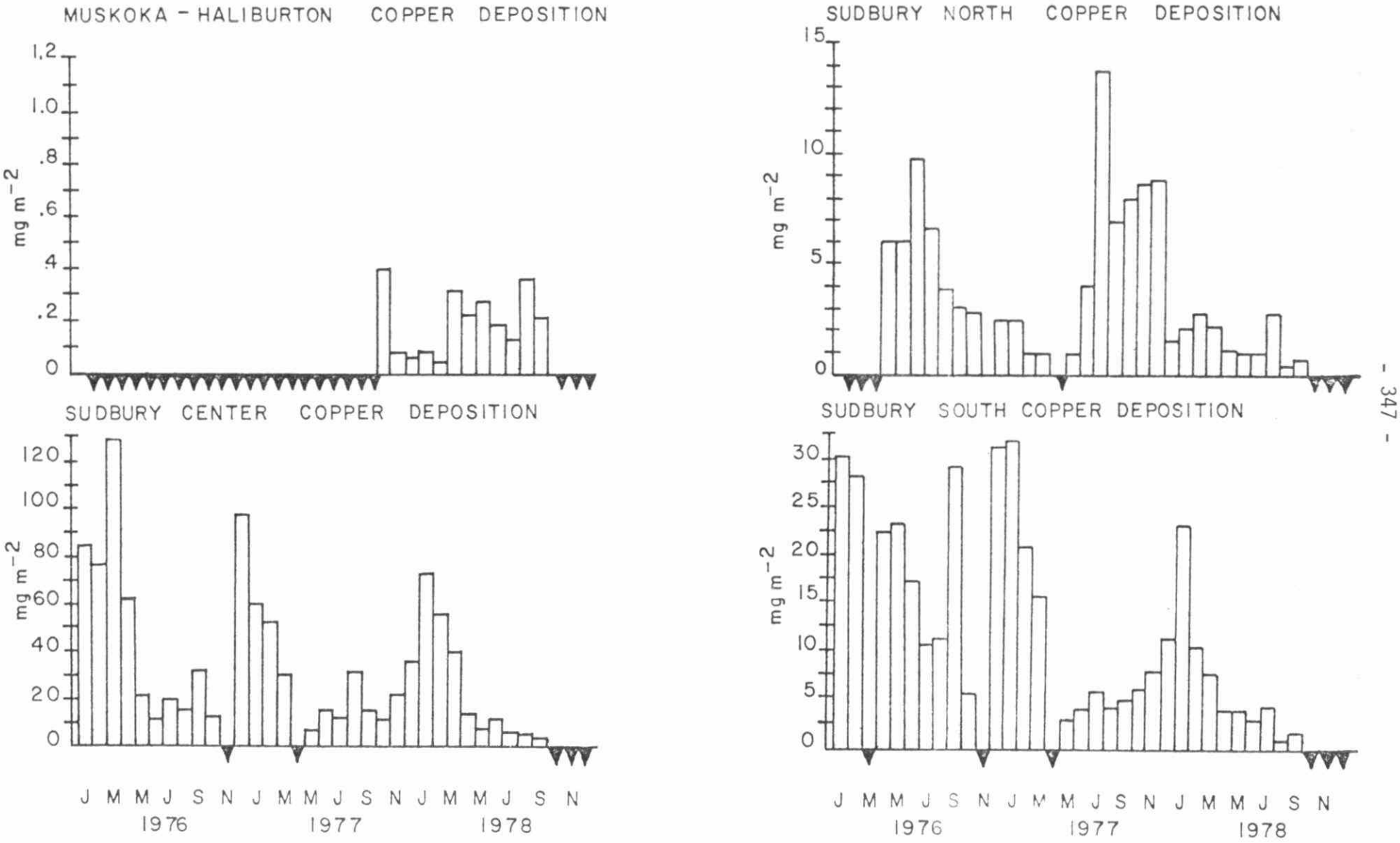

MUSKOKA - HALIBURTON COPPER DEPOSITION
mg m-2
1.2
1.0
.8
.6
.4
.2
0
SUDBURY NORTH COPPER DEPOSITION
mg m-2
15
10
5
0
SUDBURY CENTER COPPER DEPOSITION
mg m-2
120
100
80
60
40
20
0
SUDBURY SOUTH COPPER DEPOSITION
mg m-2
30
25
20
15
10
5
0
J M M J S N J M M J S N J M M J S N
1976
1977
1978

FIGURE THREE

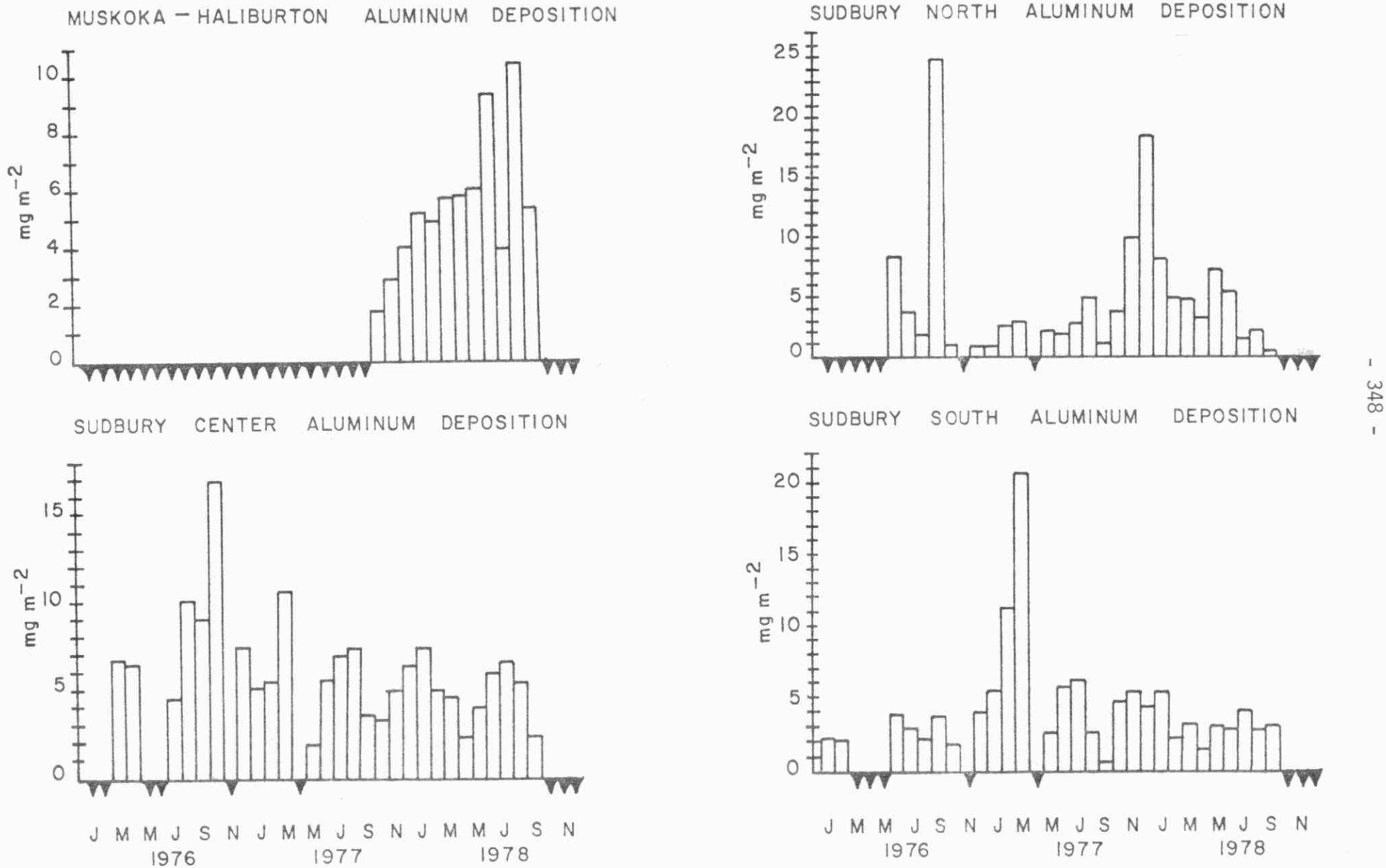


FIGURE FOUR

COPPER & NICKEL IN BULK PRECIPITATION

	Cu		Ni	
	Deposition mg $m^{-2} yr^{-1}$	CONC. ug L^{-1}	Deposition mg $m^{-2} yr^{-1}$	CONC. ug L^{-1}
Musk.–Hal.	2.33	2.8	1.7	2.
Sudb. N.	54.5	60:0	8.72	9.6
Sudb. C.	461.	501.	153.	166.
Sudb. S.	159.	173.	77.4	84.2
N. Am. Rural	4.3	9.	—	5.5
N. Am. Urb./ Ind.	15.8	—	—	—
Europe – Rural	15.	16.5	3.2	4.9
Europe – Urb. / Ind.	32.	40.	31.	35.
Grnld. / Antarc.	—	0.03–0.85	—	—

FIGURE FIVE

LEAD & ZINC IN BULK PRECIPITATION

	Pb		Zn	
	Deposition mg m^{-2} yr^{-1}	CONC. ug L^{-1}	Deposition mg m^{-2} yr^{-1}	CONC. ug L^{-1}
Musk.-Hal.	11.5	13.7	15.0	17.7
Sudb. N.	—	—	69.3	76.2
Sudb. C.	—	—	53.7	58.4
Sudb. S.	—	—	84.1	91.4
N. Am. Rural	18.2	21.	47.4	35.6
N. Am. Urb./ Ind.	101	—	238.	—
Europe — Rural	22	31.	55.	62.
Europe — Urb. / Ind.	40	49.	103.	136.
Grnld. / Antarc.	—	0.00—0.85	—	0.03-1.05

FIGURE SIX

ALUMINUM & IRON IN BULK PRECIPITATION

	Al		Fe	
	Deposition mg $m^{-2} yr^{-1}$	CONC. ug L^{-1}	Deposition mg $m^{-2} yr^{-1}$	CONC. ug L^{-1}
Musk. – Hal.	65.2	77.1	83.4	98.7
Sudb. N.	66.9	74.3	83.5	89.8
Sudb. C.	96.6	106.	1010.	1090.
Sudb. S.	51.2	56.2	384.	422.
N. Am. Rural	—	—	219.	45.
N. Am. Urb./ Ind.	—	—	2200.	—
Europe – Rural	234.	220.	165.	192.
Europe – Urb./ Ind.	620.	1060.	575.	768.
Grnld. / Antarc.	—	3.3 – 10.7	—	4.3 – 6.9

FIGURE SEVEN

METALS IN WET-ONLY PRECIPITATION

	CONCENTRATION ($\mu g\ L^{-1}$)					
	Cu	Ni	Pb	Zn	Al	Fe
MUSK – HAL.	2.26	<2.	10.6	8.85	54.7	59.8
SUDB. N.	21.7	4.03	—	12.6	11.8	23.2
SUDB. C.	82.2	29.4	—	24.3	18.3	37.7
USA (Lazrus et al) 1970	21.	4.3	34.	107.	—	—
TENNESSEE (Andren and Lindberg) 1977	14.4	5.7	15.6	34.9	—	—

FIGURE EIGHT

ENRICHMENT FACTORS FOR BULK PRECIPITATION

	ENRICHMENT FACTOR				
	Cu	Ni	Pb	Zn	Fe
MUSK – HAL.	54	<28	1200	270	1.9
SUDB. N.	1200	140	—	1200	1.8
SUDB. C.	7000	1700	—	650	15.
SUDB. S.	4600	1600	—	1900	11.

$$EF = \frac{(x / Al)\ precip.}{(x / Al)\ crust}$$

APPENDIX ELEVEN

NATIONAL ATMOSPHERIC CHEMISTRY NETWORK

Len Barrie

Included in this appendix are a map of the air and precipitation monitoring network and a sample page showing the data reporting format used.

AIR AND PRECIPITATION MONITORING NETWORK

ELA-KENORA
FEBRUARY 1979

AIR CONCENTRATIONS (10^{-6} gm^{-3})

DAY	PARTICULATE $SO_4^=$	NO_3^-	Cl^-	Na^+	K^+	NH_4^+		GAS SO_2	COMMENT
1	2.03	1.13	bdl	bdl	bdl	0.93		4.4	0
2	2.38	1.62	bdl	bdl	bdl	0.72		6.2	0
3	1.15	0.54	bdl	bdl	bdl	bdl		6.8	0
4	0.91	0.26	bdl	bdl	bdl	0.74		4.3	0
5	1.18	0.29	bdl	bdl	bdl	bdl		2.7	0
6	0.79	bdl	bdl	bdl	bdl	bdl		1.0	0
7	0.60	bdl	bdl	bdl	bdl	bdl		bdl	0
8	0.91	0.37	bdl	bdl	bdl	bdl		1.4	0
9	0.96	0.41	bdl	bdl	bdl	bdl		6.0	0
10	0.87	0.23	bdl	0.18	bdl	bdl		1.6	0
11	1.16	0.53	bdl	bdl	bdl	bdl		2.7	0
12	0.99	0.37	bdl	bdl	bdl	bdl		0.9	0
13	1.41	0.45	bdl	bdl	bdl	bdl		2.1	0
14	0.76	0.38	bdl	bdl	bdl	bdl		1.9	0
15	0.68	bdl	bdl	bdl	bdl	bdl		1.2	0
16	0.76	0.26	bdl	bdl	bdl	bdl		1.1	0
17	1.41	0.84	bdl	bdl	bdl	bdl		6.3	0
18	4.09	2.15	bdl	bdl	bdl	1.24		20.4	0
19	9.53	5.17	bdl	bdl	bdl	3.77	*	17.5	0
20	5.35	2.06	bdl	bdl	bdl	2.09	*	11.9	0
21	5.59	0.49	bdl	bdl	bdl	1.35	*	7.0	0
22	12.26	0.88	bdl	bdl	bdl	2.22	*	11.0	0
23	4.03	0.29	bdl	bdl	bdl	0.91	*	6.1	0
24	2.55	0.32	bdl	bdl	bdl	0.59	*	6.3	0
25	6.53	1.06	bdl	bdl	bdl	1.57	*	8.9	0
26	7.34	3.46	bdl	bdl	bdl	3.18	*	8.8	0
27	6.40	4.00	bdl	bdl	bdl	3.01	*	5.3	0
28	2.44	0.38	bdl	0.31	bdl	0.74	*	2.8	0
NO. OBS.	28	28	-	-	-	28		28	
A. MEAN	3.04	1.00	-	-	-	0.82		5.6	
S.D.	3.04	1.28	-	-	-	1.11		4.9	
MIN.	0.60	bdl	-	-	-	bdl		bdl	
MAX.	12.26	5.17	-	-	-	3.77		20.4	
MEAN (dl)	3.04	0.94	-	-	-	0.13		5.5	

bdl - BELOW DETECTION LIMIT

* BLANK IS GREATER THAN 2 STANDARD DEVIATIONS ABOVE MEAN

PRECIPITATION CONCENTRATIONS

(10^{-3} gl^{-1})

DAY	AMOUNT STD (mm)	AMOUNT COLL (mm)	pH FIELD	pH LAB	$SO_4^=$	NO_3^-	Cl^-	Ca^{++}	NH_4^+	Mg^{++}	Na^+	K	TOT P	ION BAL. RATIO +VE/-VE	PRECIP TYPE	COMMENT
3	1.5	1.0	-	-	1.4	1.505	0.5	0.23	0.052	0.03	-	-	-	-	2	0
4	1.8	1.0	-	-	2.8	0.443	1.8	0.40	0.077	0.14	-	-	-	-	2	0
5	2.6	1.3	-	-	1.0	0.841	0.4	0.18	0.013	0.02	0.25	0.17	-	-	2	0
6	1.4	1.0	-	-	1.2	-	0.4	-	-	-	-	-	-	-	2	0
10	0.8	1.0	-	-	2.4	1.638	1.6	0.24	0.258	0.02	0.75	1.30	-	-	2	0
11	0.9	2.1	-	5.80	1.3	0.443	0.4	0.18	0.039	0.02	0.55	0.17	-	0.87	2	0
13	2.8	5.5	-	5.10	5.4	0.487	3.6	0.03	0.026	bdl	0.10	0.04	-	-	2	0
20	0.4	0.8	-	-	2.4	1.726	0.5	0.12	0.116	0.01	1.25	0.15	-	-	2	0
21	0.4	0.7	-	-	17.2	-	13.2	-	-	-	-	-	-	-	2	0
22	12.8	8.3	4.78	4.80	1.1	0.708	0.2	0.03	0.090	0.01	0.06	0.12	0.009	0.72	2	0
23	1.2	0.4	-	-	1.0	-	2.7	-	-	-	0.28	2.80	-	-	2	0
28	2.4	1.1	-	-	1.1	2.966	0.9	-	0.206	-	0.46	0.61	-	-	2	0
NO. OBS.	12	12	-	-	12	-	12	-	-	-	-	-	-	-		
A. MEAN	2.4	2.0	-	-	3.2	-	2.2	-	-	-	-	-	-	-		
STD. DEV.	3.4	2.4	-	-	4.6	-	3.6	-	-	-	-	-	-	-		
MINIMUM	0.4	0.4	-	-	1.0	-	0.2	-	-	-	-	-	-	-		
MAXIMUM	12.8	8.3	-	-	17.2	-	13.2	-	-	-	-	-	-	-		
P.W. MEAN			-	-	1.9	-	1.1	-	-	-	-	-	-	-		
A. MEAN dl					3.2	-	2.2	-	-	-	-	-	-			
PW MEAN dl					1.9	-	1.1	-	-	-	-	-	-			

PRECIP TYPE
1 - RAIN
2 - SNOW
3 - MIXED
4 - UNCERTAIN

T - TRACE AMOUNT

APPENDIX TWELVE

GREAT LAKES BASIN - THE CANSAP NETWORK

Doug Whelpdale

Included in this appendix are various related maps, diagrams, and graphs.

Figure One

United States Portion of WMO / NOAA / EPA Precipitation Chemistry Network

Figure Two

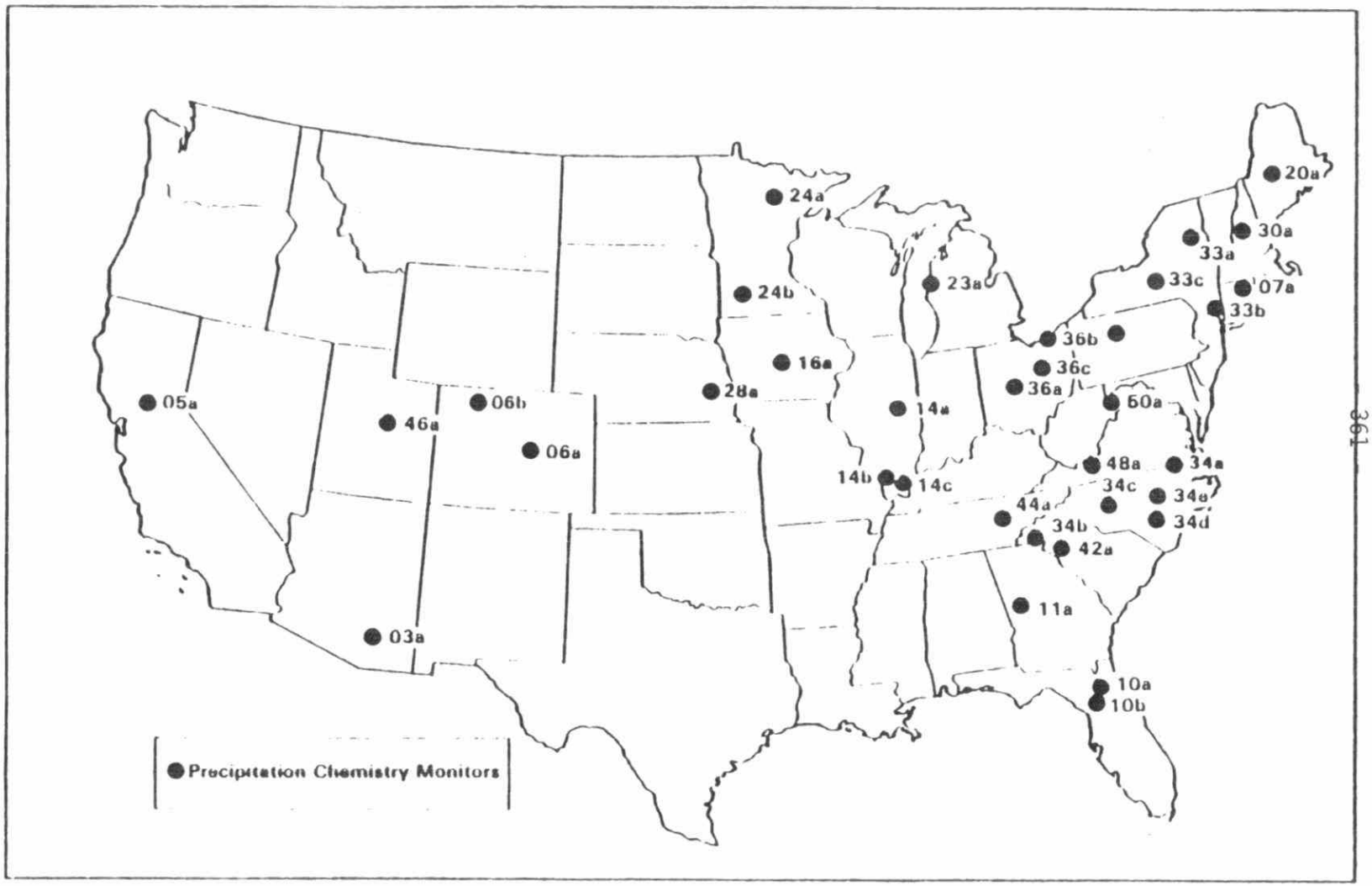
Electric Power Research Institute (EPRI) Precipitation Chemistry Monitoring Network

Figure Three

EPA/DOE Multi-State Atmospheric Power Production Pollution Study Precipitation Chemistry Network (MAP3S)

Figure Four

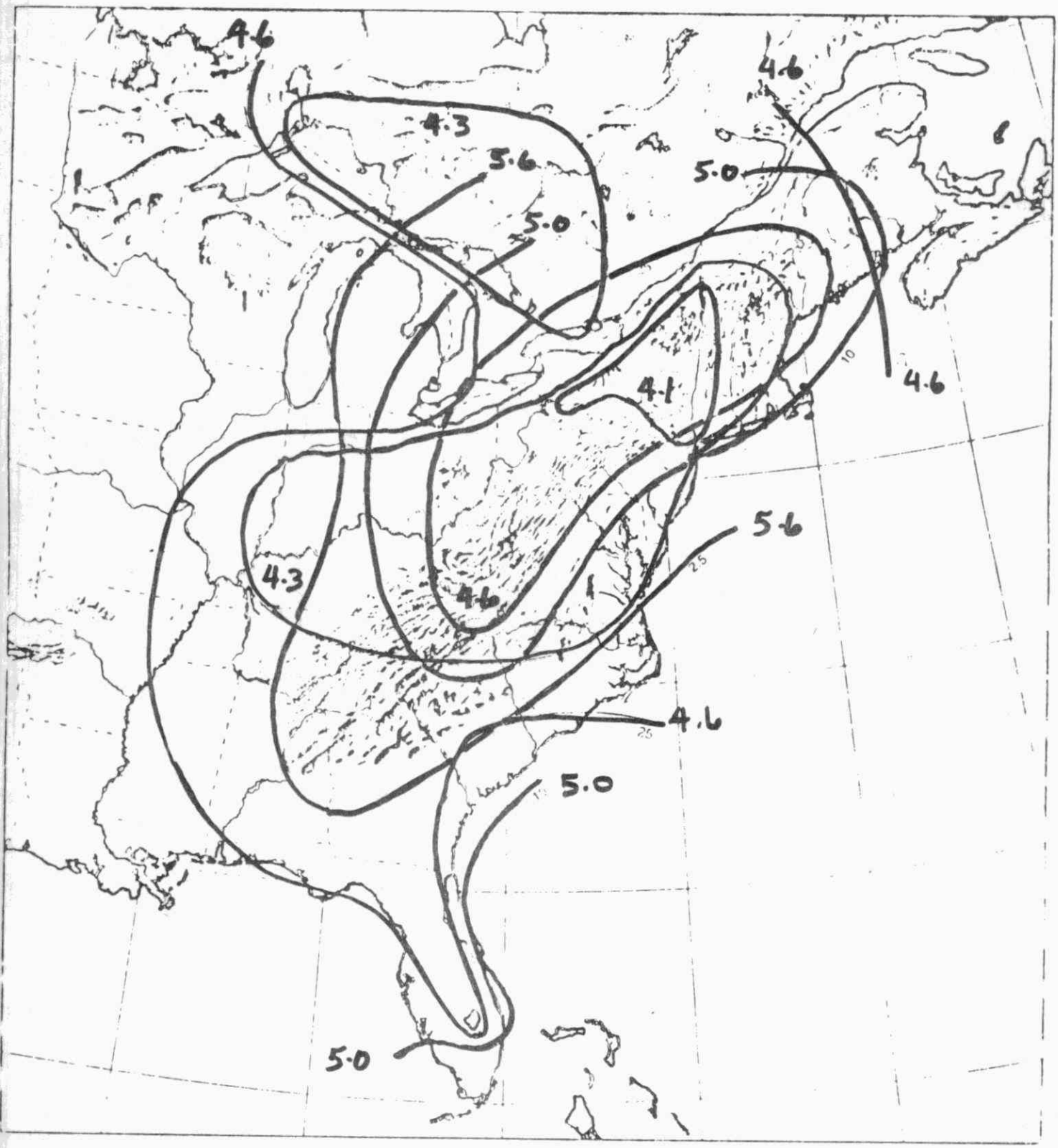
National Atmospheric Deposition Project Network (NC141)



... and human activity come from this one area. The complex. During the past ... to the annual emissions of sulfur from Sudbury have about equaled the amount thought to have been emitted by all the volcanoes of the world.

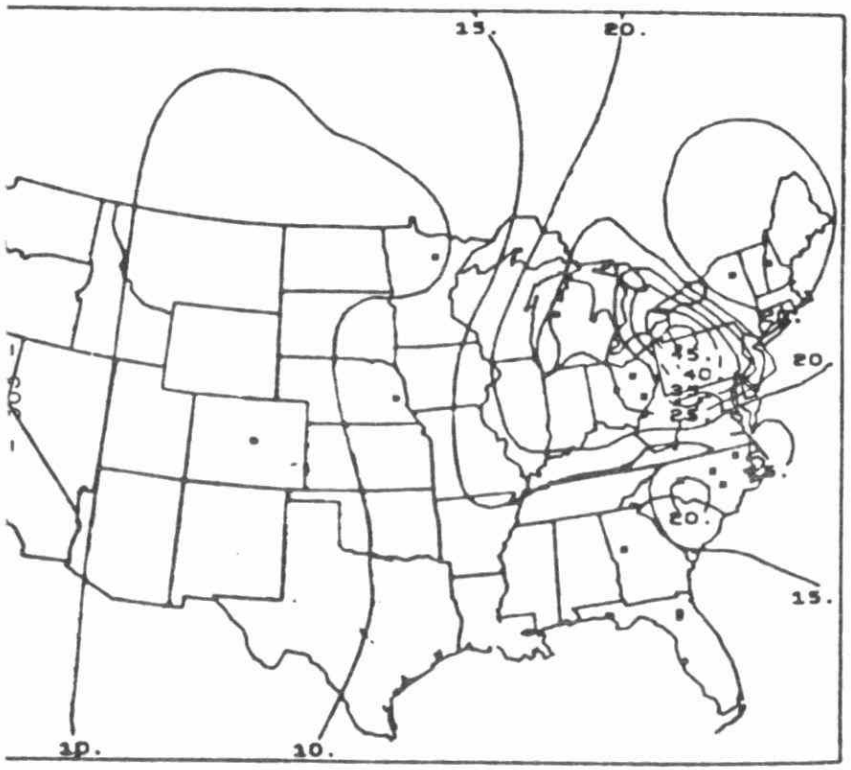
It is beyond argument that such pollutants ... transported over long distances through the atmosphere. Studies of the deposition of sulfur, lead and other matter ... on the Greenland ice cap and in other remote places demonstrate such mechanisms of dispersal. What is a matter of sometimes heated discussion, particularly when ... alleged foreign pollution is causing a political bout, is the ... proportion of pollutant ... can be attributed to remote sources.

On an annual basis rain and snow over large regions of the world are now from five to 10 times more acid than the low

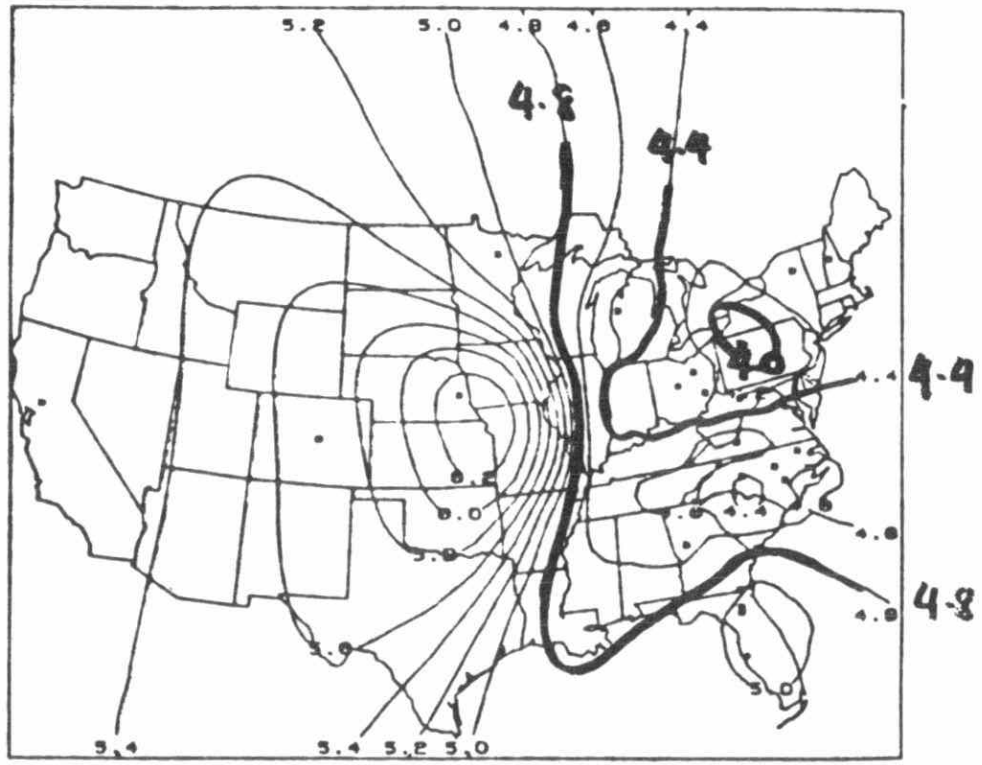


SPREAD OF ACID RAIN in eastern North America is depicted for 1955–56 (*black*) and 1975–76 (*color*) with data for the isolines based on the concentration of hydrogen ions in microequivalents per liter. The quality of the data for North America is variable and the sampling methods employed for the two periods represented on this map were somewhat different, but the general pattern and trend are clear. Areas sensitive to acid rain and snow are also shown. Similar areas are found farther north in Canada and in the Rocky Mountains. They have a low ability to neutralize acids. Values higher than 2.5

Figure Five



JRED CONDUCTIVITY(UMHO/CM) MEDIAN
ONAL ATMOSPHERIC DEPOSITION PROGRAM (NADP)
- ILLINOIS STATE WATER SURVEY
: 29 JUN 79 WET SIDE. CAL LAB TYPE- W



MEASURED PH MEDIAN
NATIONAL ATMOSPHERIC DEPOSITION PROGRAM (NADP)
CAL - ILLINOIS STATE WATER SURVEY
DATE: 29 JUN 79 WET SIDE. CAL LAB TYPE- W

Figure Six

Figure Seven

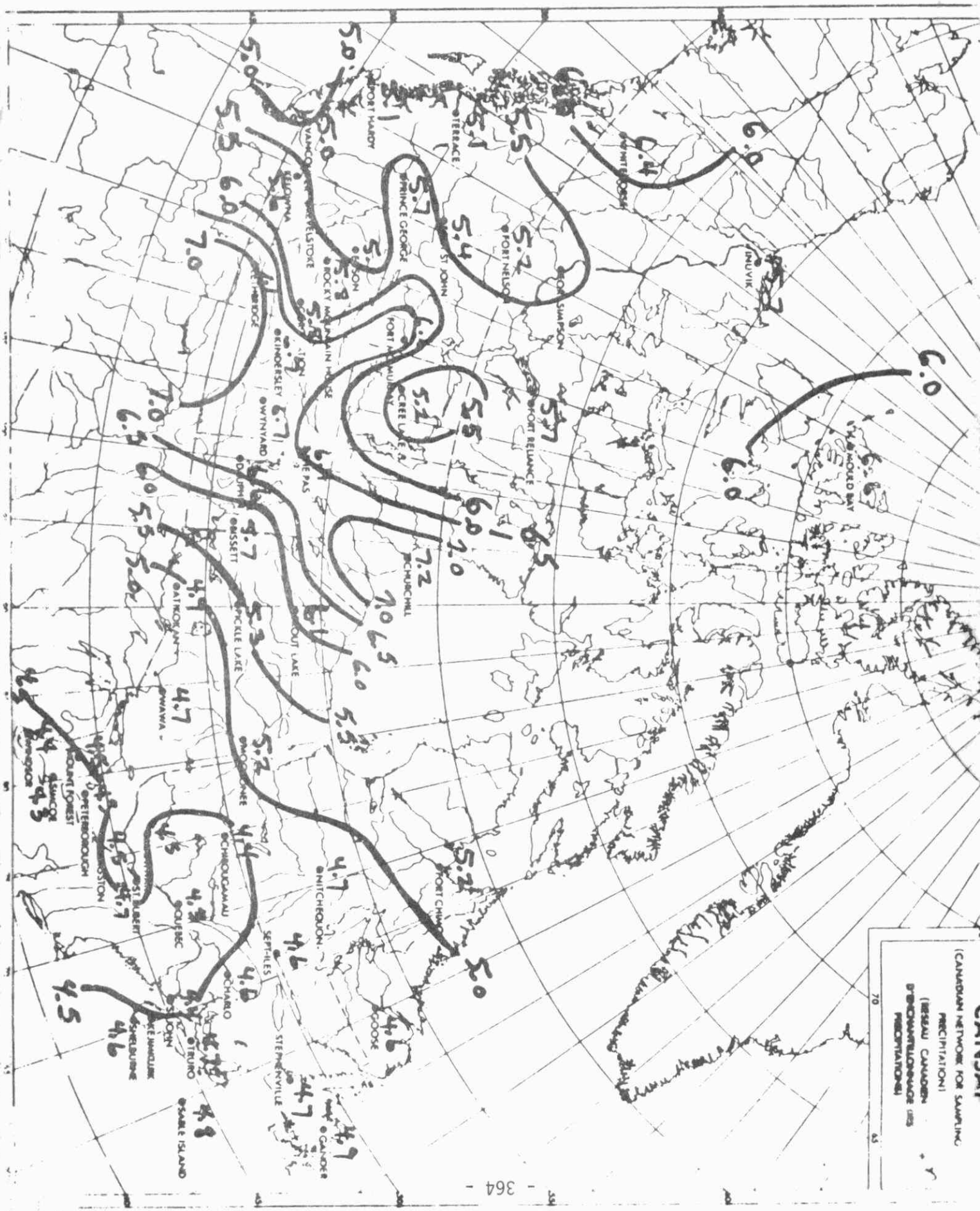
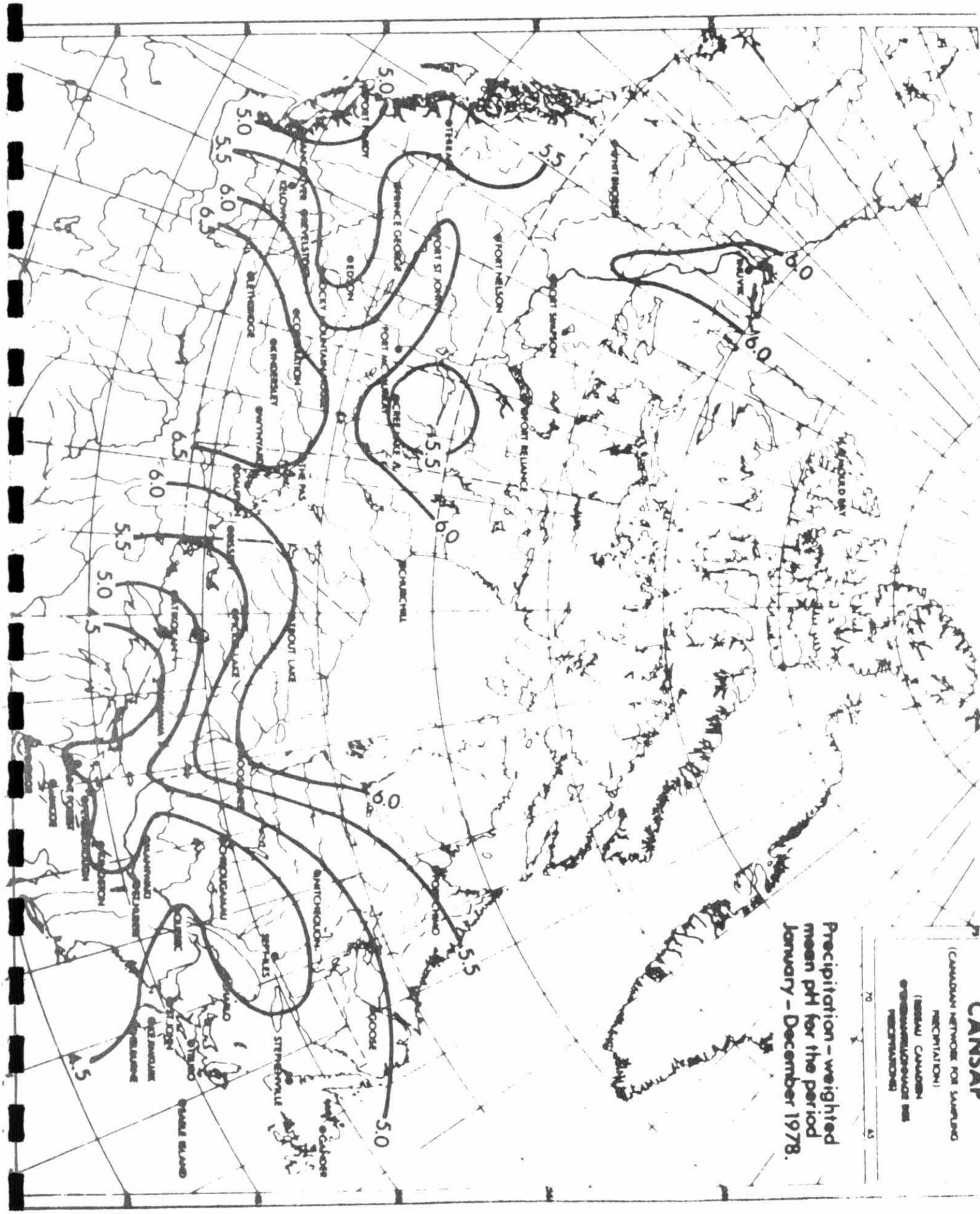
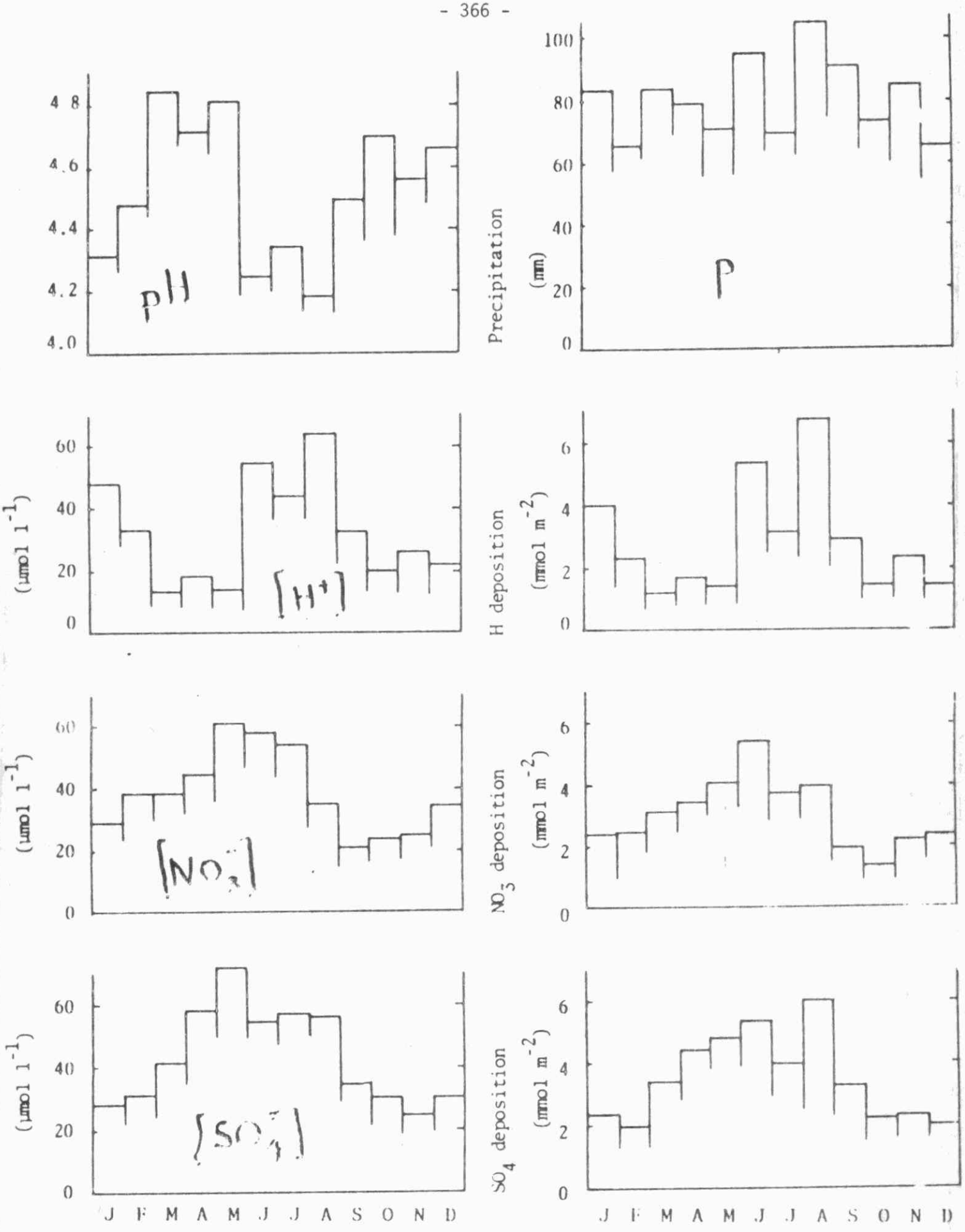


Figure Eight





Mean monthly concentration and deposition at Mount Forest, Ontario for July 1972 to April 1978.

Figure Nine

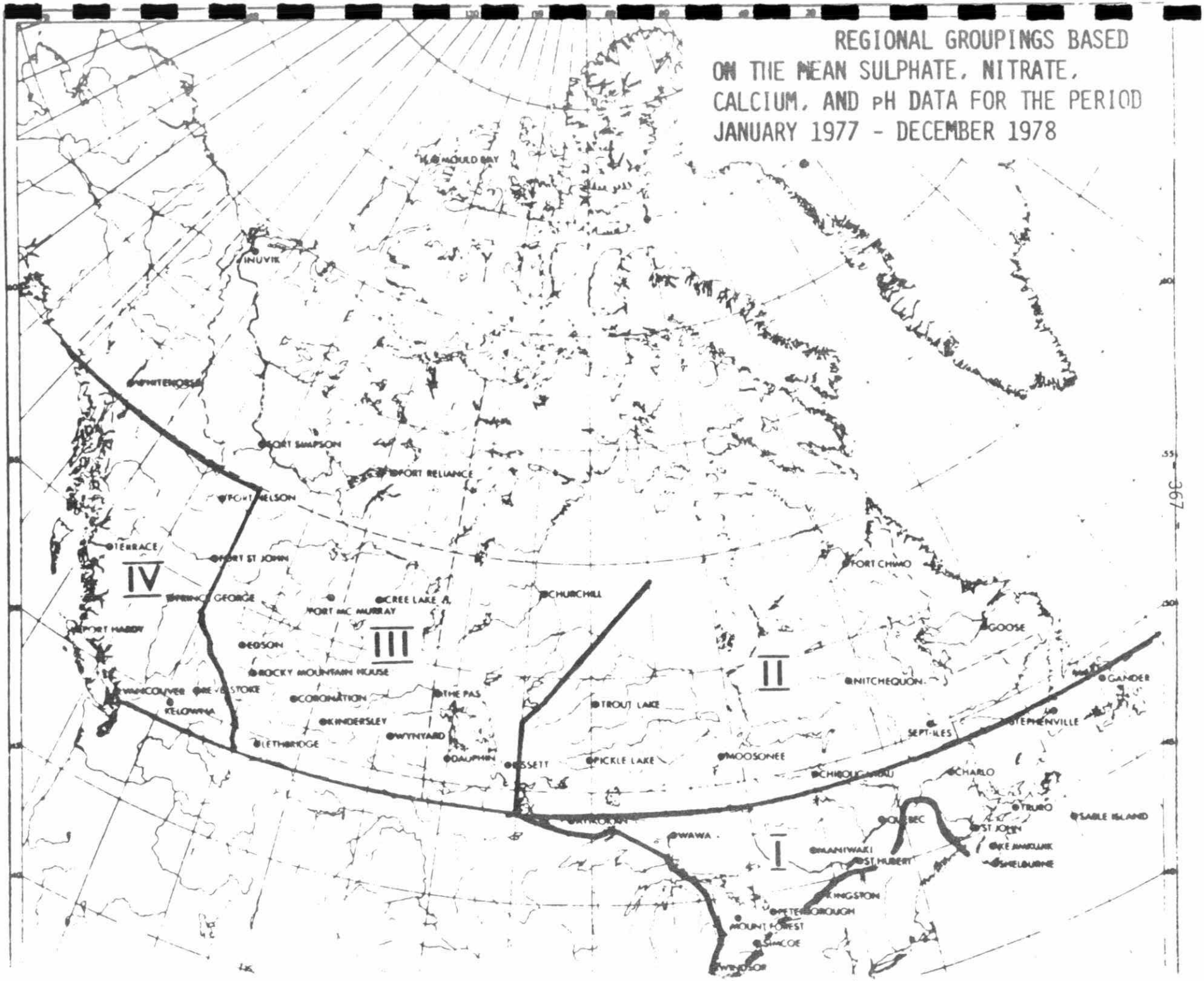
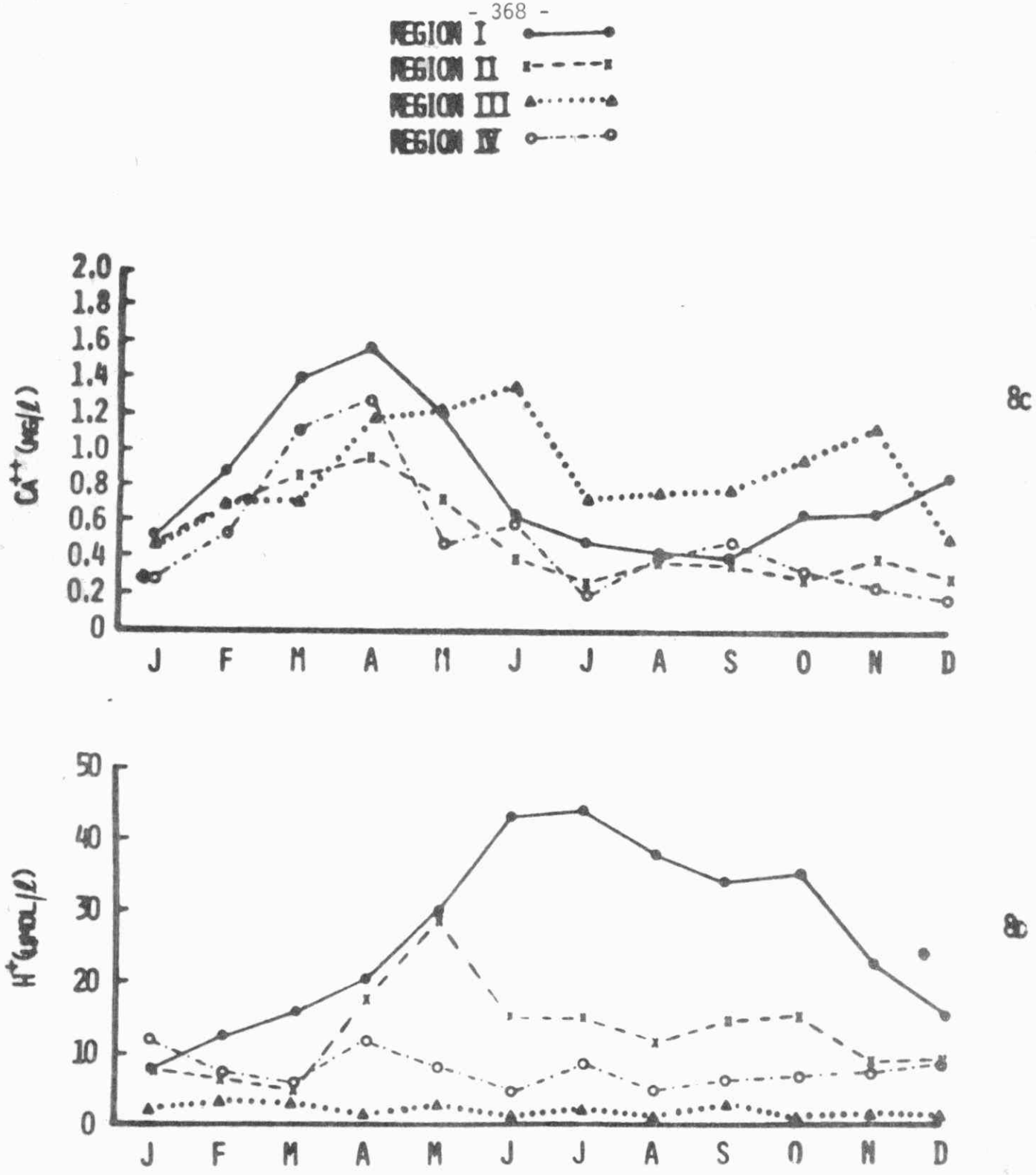
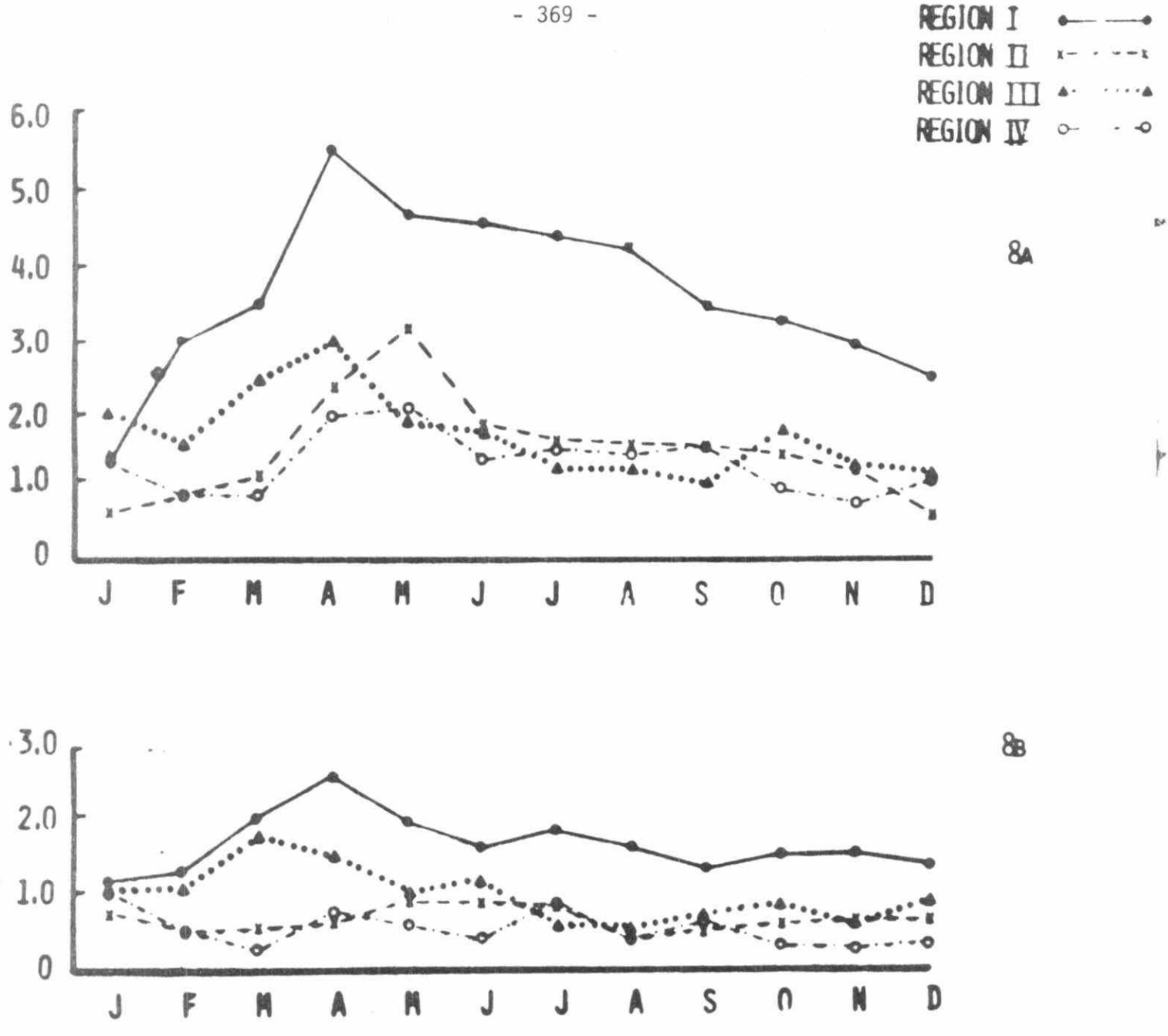

REGIONAL GROUPINGS BASED
ON THE MEAN SULPHATE, NITRATE,
CALCIUM, AND pH DATA FOR THE PERIOD
JANUARY 1977 - DECEMBER 1978
IV
III
II
I
MOULD BAY
INUVIK
WHITEHORSE
FORT SIMPSON
FORT RELIANCE
FORT NELSON
TERRACE
FORT ST JOHN
PRINCE GEORGE
FORT HARDY
CREE LAKE A.
FORT McMURRAY
EDSON
ROCKY MOUNTAIN HOUSE
VANCOUVER
REVELSTOKE
KELOWNA
CORONATION
THE PAS
KINDERSLEY
WYNYARD
LETHBRIDGE
DAUPHIN
ESSETT
PICKLE LAKE
TROUT LAKE
CHURCHILL
FORT CHIMO
GOOSE
NITCHEQUON
GANDER
STEPHENVILLE
SEPT-ILES
MOOSONEE
CHIBOUGAMAU
CHARLO
TRURO
SABLE ISLAND
QUEBEC
ST JOHN
KEJIMKUJIK
SHELBURNE
WAWA
MANIWAKI
ST HUBERT
KINGSTON
PETERBOROUGH
MOUNT FOREST
SIMCOE
WINDSOR

Figure Ten



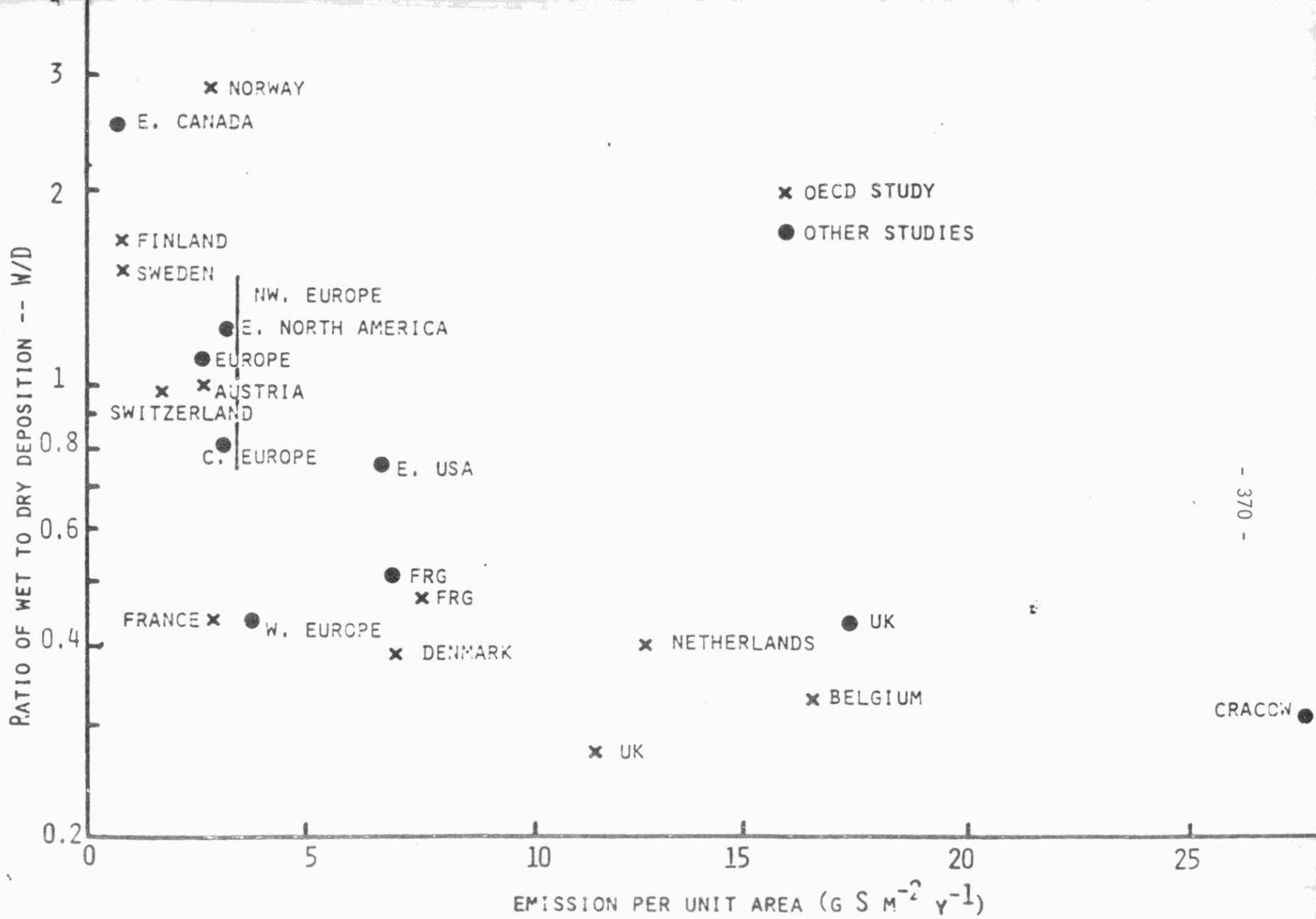
MONTHLY PRECIPITATION - WEIGHTED AREAL MEAN CONCENTRATIONS OF A) SULPHATE, B) NITRATE, C) CALCIUM, D) HYDROGEN ION FOR THE CANSAP DATA FOR THE PERIOD JANUARY 1977 - DECEMBER 1978

Figure Eleven



MONTHLY PRECIPITATION - WEIGHTED AREAL MEAN CONCENTRATIONS OF A) SULPHATE, B) NITRATE, C) CALCIUM, D) HYDROGEN ION FOR THE CANSAP DATA FOR THE PERIOD JANUARY 1977 - DECEMBER 1978

Figure Twelve



RELATIVE IMPORTANCE OF WET AND DRY DEPOSITION AS A FUNCTION OF EMISSION DENSITY.

Figure Thirteen

APPENDIX THIRTEEN

GREAT LAKES BASIN - THE CCIW NETWORK

C. H. Chan

OBJECTIVES

1. TO ESTIMATE THE CONTRIBUTION OF THE ATMOSPHERE TO THE CHEMICAL BUDGET OF THE GREAT LAKES

2. TO ESTABLISH LONG TERM RECORDS OF CHEMICAL COMPOSITION IN THE ATMOSPHERIC PRECIPITATION IN THE GREAT LAKES BASIN

TABLE 1

CHEMICAL PARAMETERS

Reactive Phosphate

Total Phosphorus

Nitrate + Nitrite

Ammonia

Total Nitrogen

Silica

Sulphate

Chloride

Sodium

Potassium

Calcium

Magnesium

Lead

Zinc

Iron

Copper

Nickel

Cadmium

Conductivity

BULK PRECIPITATION SAMPLER

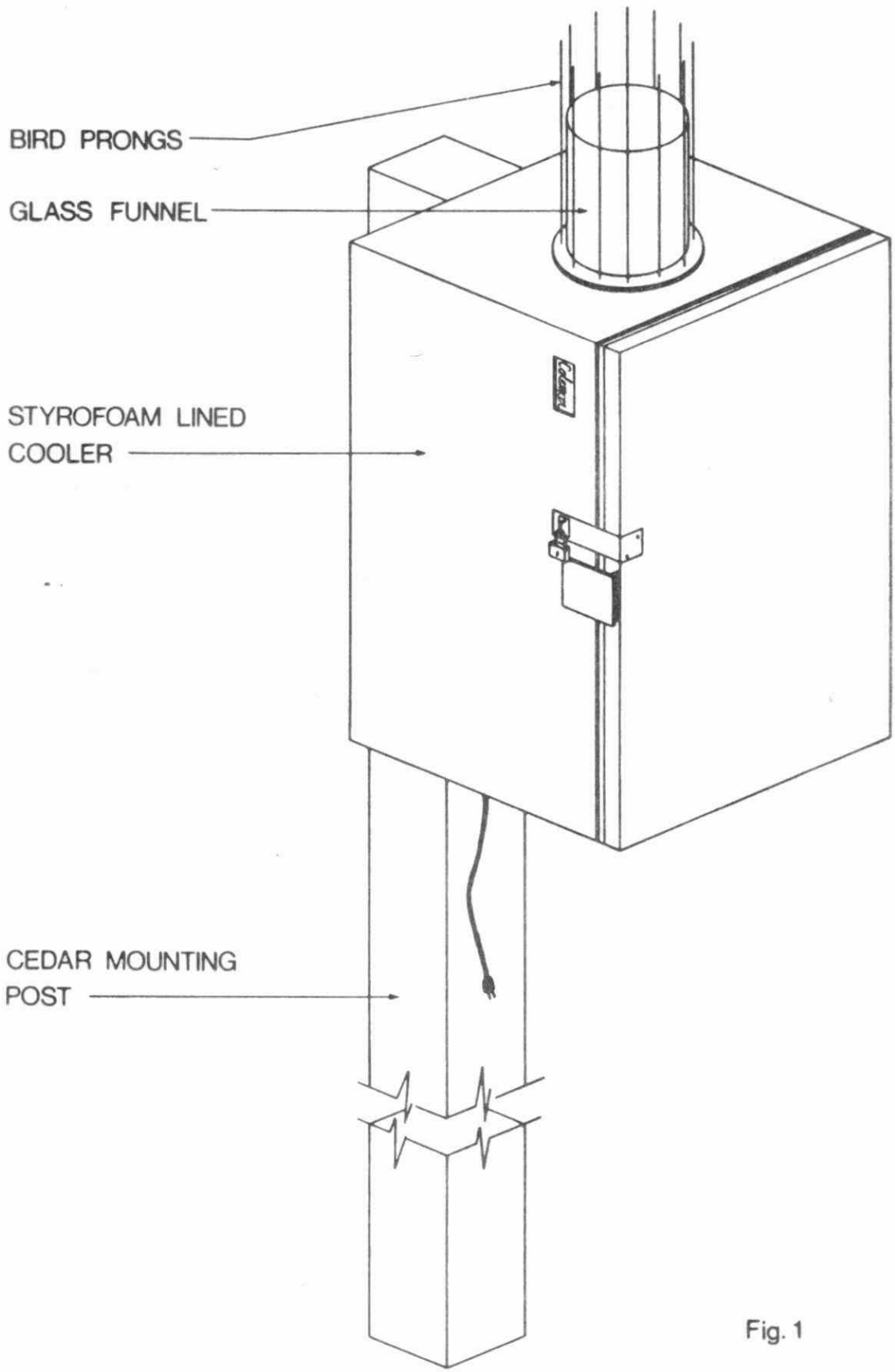


Fig. 1

BULK PRECIPITATION SAMPLER INTERIOR

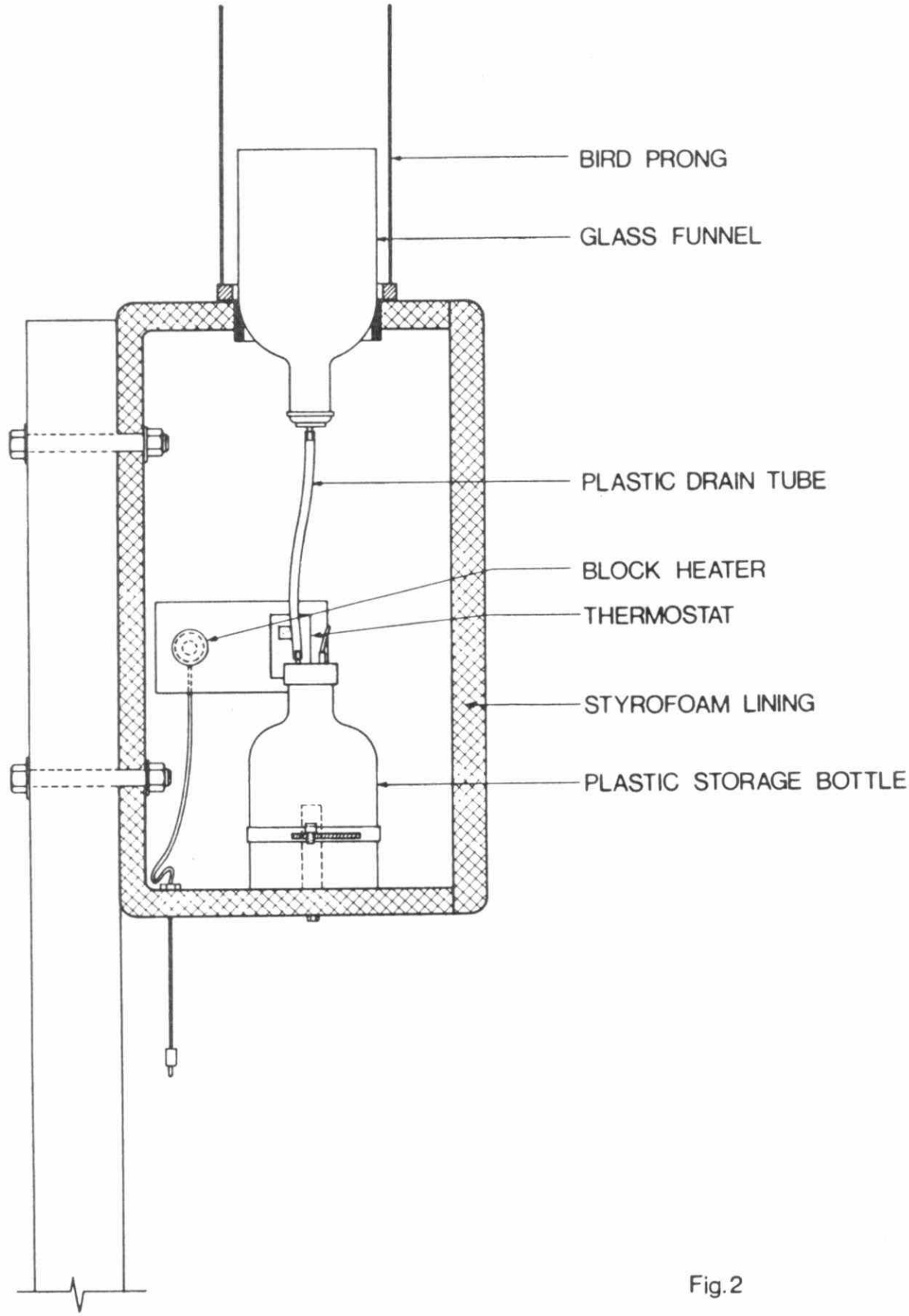


Fig.2

PRECIPITATION COLLECTOR

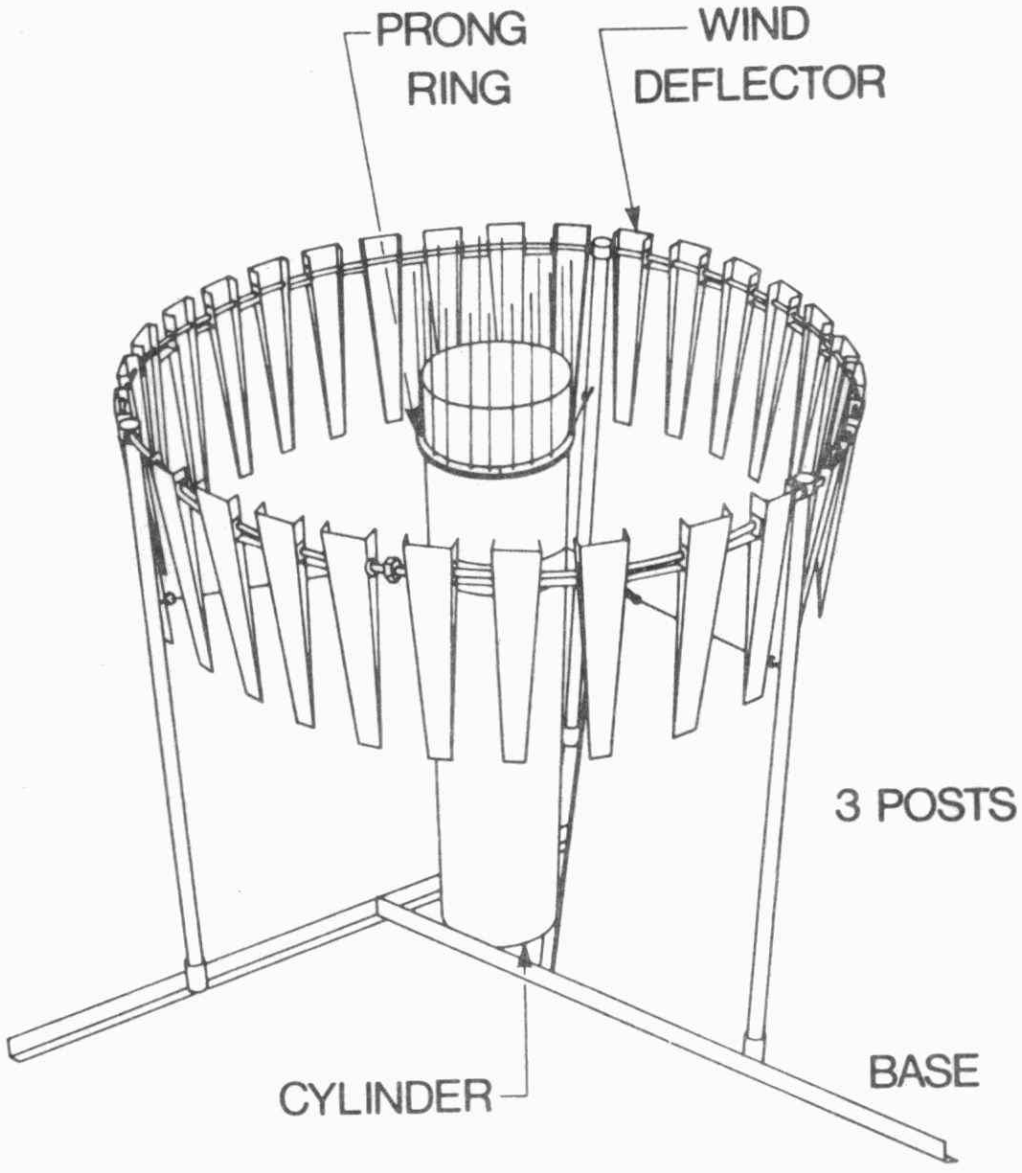
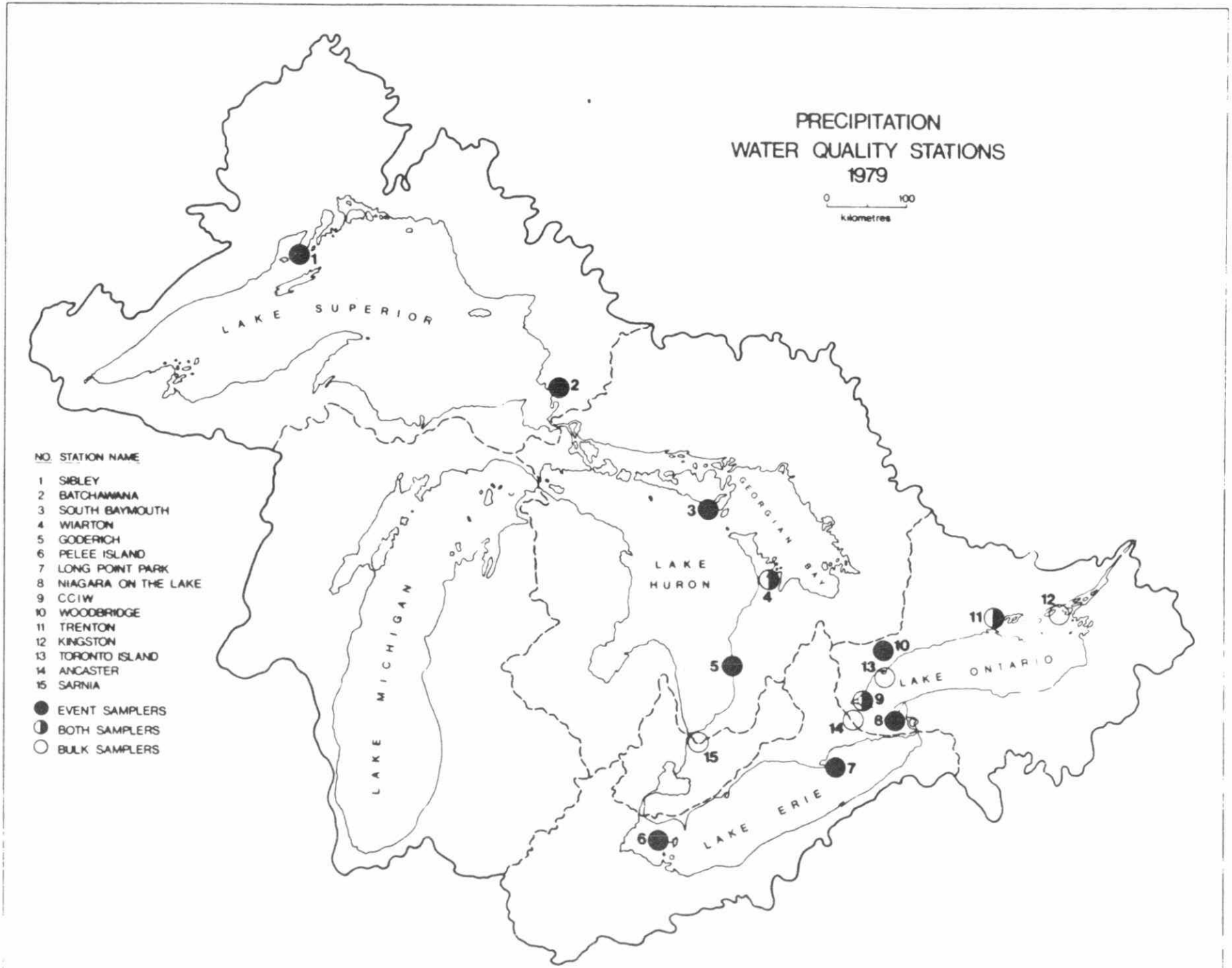


Fig. 3


PRECIPITATION
WATER QUALITY STATIONS
1979
0
100
kilometres
LAKE SUPERIOR
LAKE MICHIGAN
LAKE HURON
GEORGIAN BAY
LAKE ONTARIO
LAKE ERIE
NO. STATION NAME
1 SIBLEY
2 BATCHAWANA
3 SOUTH BAYMOUTH
4 WIARTON
5 GODERICH
6 PELEE ISLAND
7 LONG POINT PARK
8 NIAGARA ON THE LAKE
9 CCIW
10 WOODBRIDGE
11 TRENTON
12 KINGSTON
13 TORONTO ISLAND
14 ANCASTER
15 SARNIA
EVENT SAMPLERS
BOTH SAMPLERS
BULK SAMPLERS

TYPES OF SAMPLER

LOCATION	RAIN	SNOW	SANGAMO
SIBLEY			1977
BATCHAWANA			1976
S. BAY MOUTH			1977
WIARTON		1977	1977-
GODERICH			1977-
SARNIA	1971 1975	1973	
PT. PELEE	1970-1976	1773-1976	1977-
LONG POINT			1979
NIAGARA			1977
BURLINGTON	1969-	1972-	1975-
ANCASTER	1970-		
TORONTO	1970	1973	
WOODBRIGDE	1969	1973	1979
TRETON	1969 1977	1973	1978
KINGSTON	1969	1973	1978

1972 — 1977

LAKE ONTARIO PRECIPITATION (RAIN SAMPLER)

		1972	1973	1974	1975	1976	1977
VOL.	KIN.	827	715	609	706	779	638
	TRE.	722	694	592	582	449	488
	W.B.	587	518	486	419	691	791
	TOR.	790	642	623	856	621	900
	CCIW	770	683	605	762	664	778
pH.	KIN.	6.71	6.02	4.90	5.27	4.63	4.47
	TRE.	6.69	6.30	4.83	4.82	4.68	4.68
	W.B.	6.38	6.08	5.28	5.10	4.56	5.02
	TOR.	6.05	5.74	5.71	4.84	4.56	4.84
	CCIW.	6.97	6.38	5.54	6.00	5.54	6.59
COND.	KIN.	33.	47.	57.	46.	48.	54.
	TRE.	39.	48.	54.	37.	62.	127.
	W.B.	39.	82.	70.	48.	42.	38.
	TOR.	40.	85.	76.	60.	152.	51.
	CCIW.	90.	124.	146.	184.	157.	99
T.P.	KIN.	74.	89.	132.	131.	27.	108.
	TRE.	14.	16.	43.	41.	60.	74.
	W.B.	12.	351.	36.	45.	26.	39.
	TOR.	20.	96.	266.	84.	54.	31.
	CCIW.	28.	109.	291.	258.	201.	320.
NO_3.	KIN.	0.92	1.23	0.95	1.25	1.02	0.94
	TRE.	1.18	0.99	1.01	0.97	1.29	1.49
	W.B.	1.22	1.23	0.91	1.10	1.03	1.10
	TOR.	1.31	1.32	1.69	1.27	1.44	0.98
	CCIW.	1.29	1.22	1.53	1.17	1.70	1.40

1972–1977

LAKE ONTARIO PRECIPITATION (RAIN SAMPLE

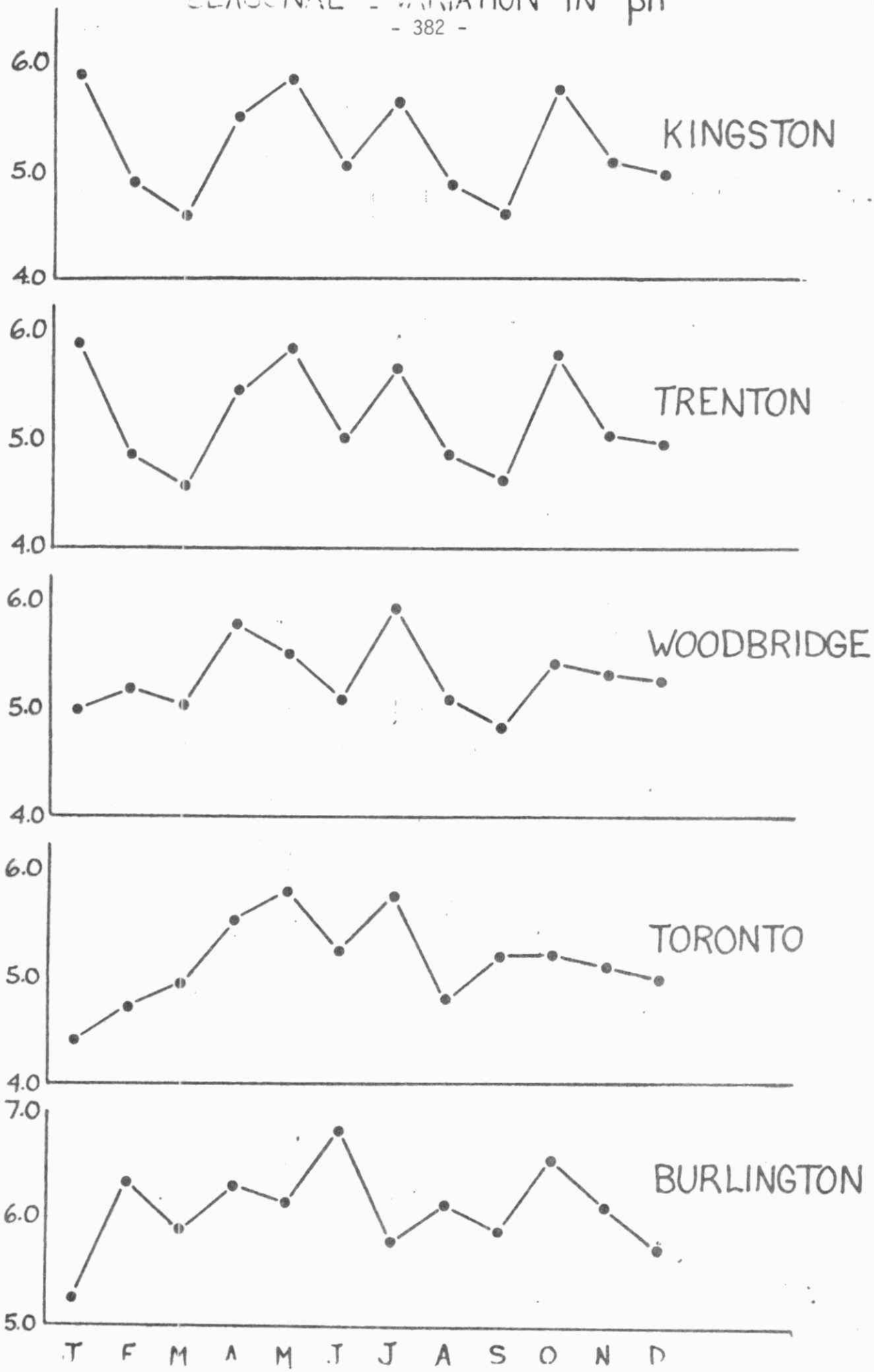
		1972	1973	1974	1975	1976	1977
NH_3.	KIN.	0.61	0.75	0.52	1.19	0.57	0.73
	TRE.	0.48	0.36	0.64	0.62	48.1	0.99
	W.B.	0.36	0.78	0.50	0.70	0.68	0.78
	TOR.	0.48	0.46	1.39	0.93	0.76	0.69
	C.C.I.W.	0.58	0.93	1.66	1.75	1.47	2.00
SiO_2.	KIN.	3.60	1.95	0.80	1.4	0.08	0.07
	TRE.	4.20	1.87	0.66	0.09	0.10	0.12
	W.B.	3.36	3.09	1.65	0.09	0.08	0.07
	TOR.	2.13	2.64	1.54	0.13	0.22	0.13
	C.C.I.W.	3.82	3.00	1.34	0.29	0.64	0.28
NA.	KIN.	1.48	1.55	0.68	0.24	0.17	0.19
	TRE.	1.49	1.06	0.77	0.19	0.32	8.01
	W.B.	1.42	1.63	1.09	0.62	0.40	0.40
	TOR.	1.27	1.77	1.49	0.84	0.74	0.64
	C.C.I.W.	12.27	4.35	11.93	30.74	13.81	7.62
CA.	KIN.	2.77	3.72	1.89	2.09	2.14	1.53
	TRE.	3.23	3.95	2.24	1.81	3.00	2.94
	W.B.	2.94	3.76	2.43	2.39	1.70	1.86
	TOR.	3.19	7.50	3.83	2.47	6.95	5.27
	C.C.I.W.	4.76	5.77	5.55	3.85	4.12	4.54
Mg.	KIN.	0.54	0.54	0.26	0.22	0.16	0.17
	TRE.	0.49	0.37	0.21	0.12	0.18	0.23
	W.B.	0.71	0.80	0.48	0.62	0.40	0.52
	TOR.	0.45	0.74	0.64	0.50	1.12	0.48
	C.C.I.W.	1.03	0.99	1.05	0.77	0.75	0.94

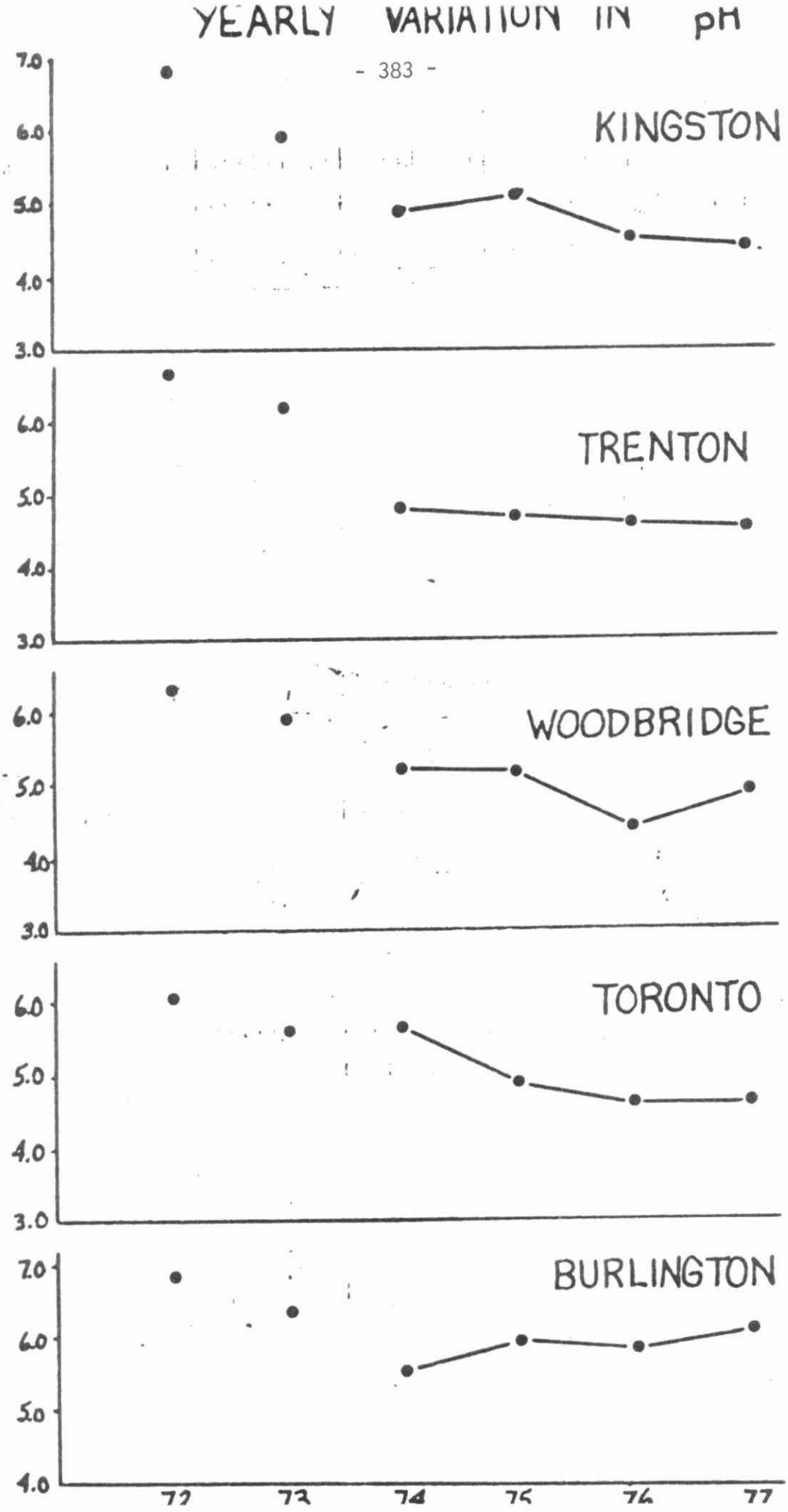
1972 -- 1977

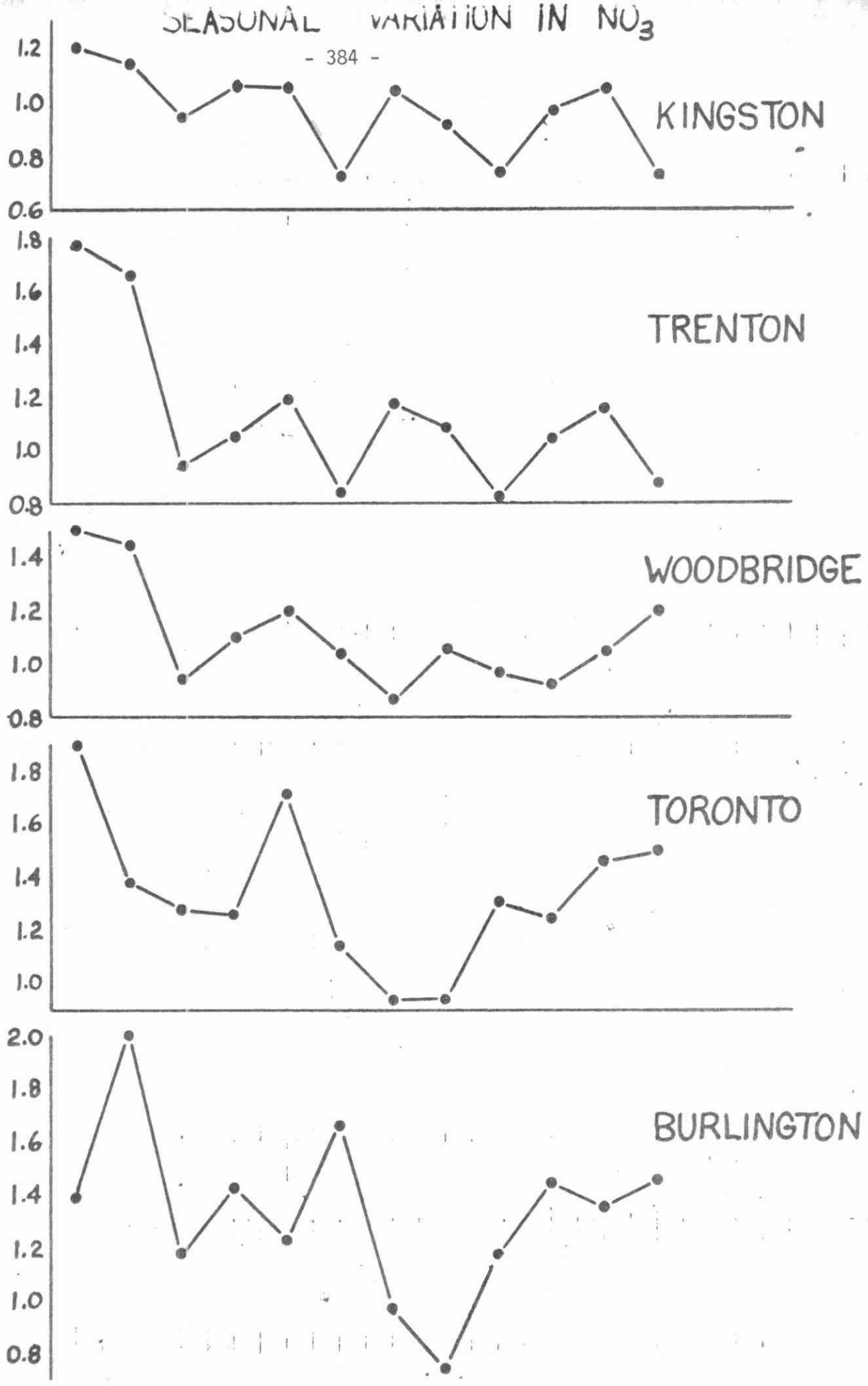
LAKE ONTARIO PRECIPITATION (RAIN SAMPLE

		1972	1973	1974	1975	1976	1977
K	KIN.	0.38	0.36	0.17	0.22	0.12	0.20
	TRE.	0.25	0.20	0.24	0.12	0.26	0.29
	W.B.	0.27	0.49	0.13	0.13	0.09	0.13
	TOR.	0.45	0.20	0.49	0.18	0.17	0.16
	C.C.I.W.	0.35	0.33	0.54	0.43	0.46	0.63
Cl.	KIN.	0.45	2.83	3.63	1.75	1.54	1.9
	TRE.	0.59	2.25	2.79	1.15	3.15	17.8
	W.B.	1.70	4.39	6.24	4.56	1.89	1.34
	TOR.	1.09	3.78	6.25	3.42	20.17	2.33
	C.C.I.W.	12.34	8.24	14.13	39.13	23.79	12.47
SO_4	KIN.	5.34	6.80	4.97	6.31	5.49	5.89
	TRE.	6.52	6.30	5.34	5.45	6.23	7.67
	W.B.	7.85	8.52	5.56	6.05	5.79	5.85
	TOR.	7.83	10.70	8.90	7.08	11.05	6.78
	C.C.I.W.	9.69	10.19	11.01	9.49	10.17	9.77

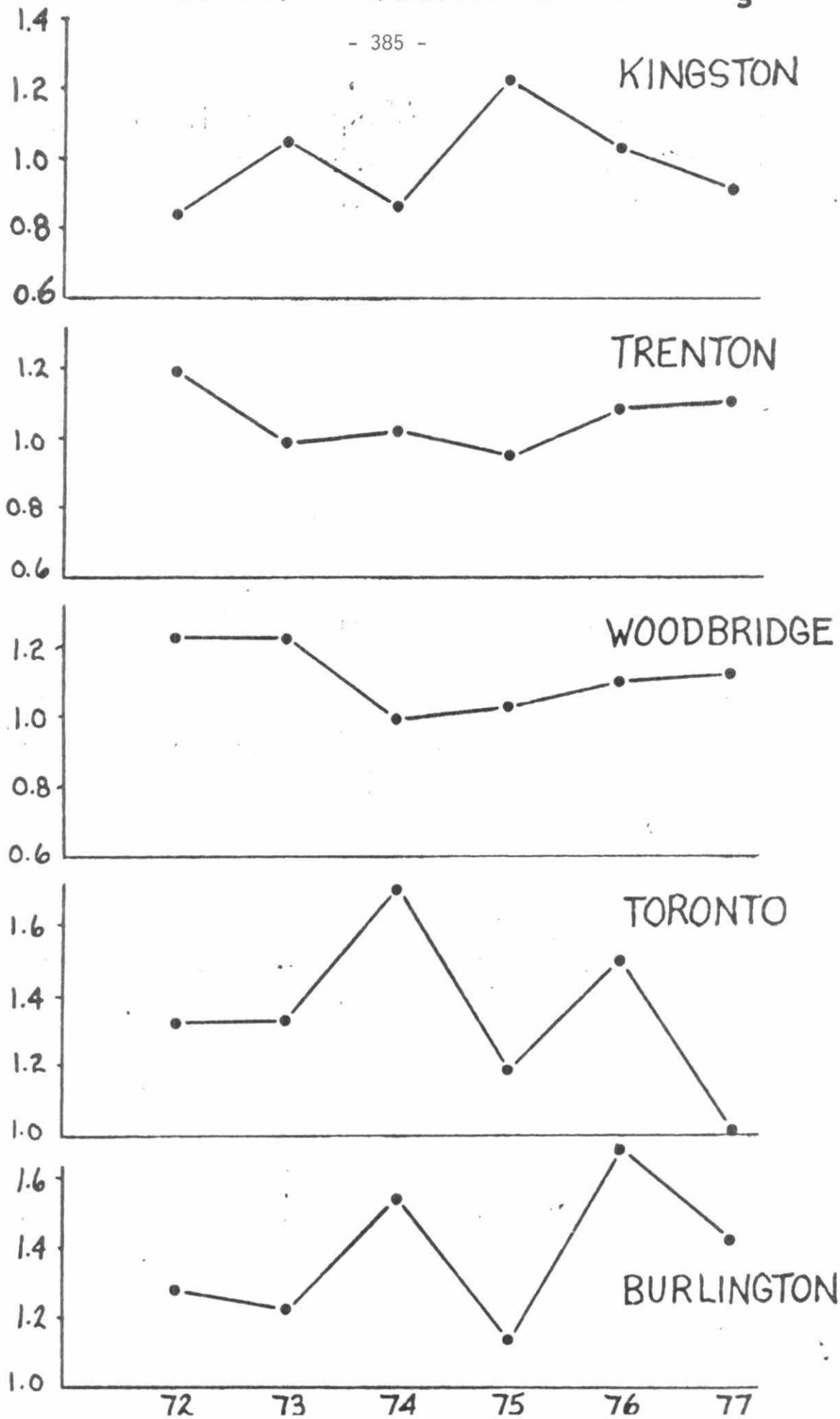
SEASONAL VARIATION IN pH

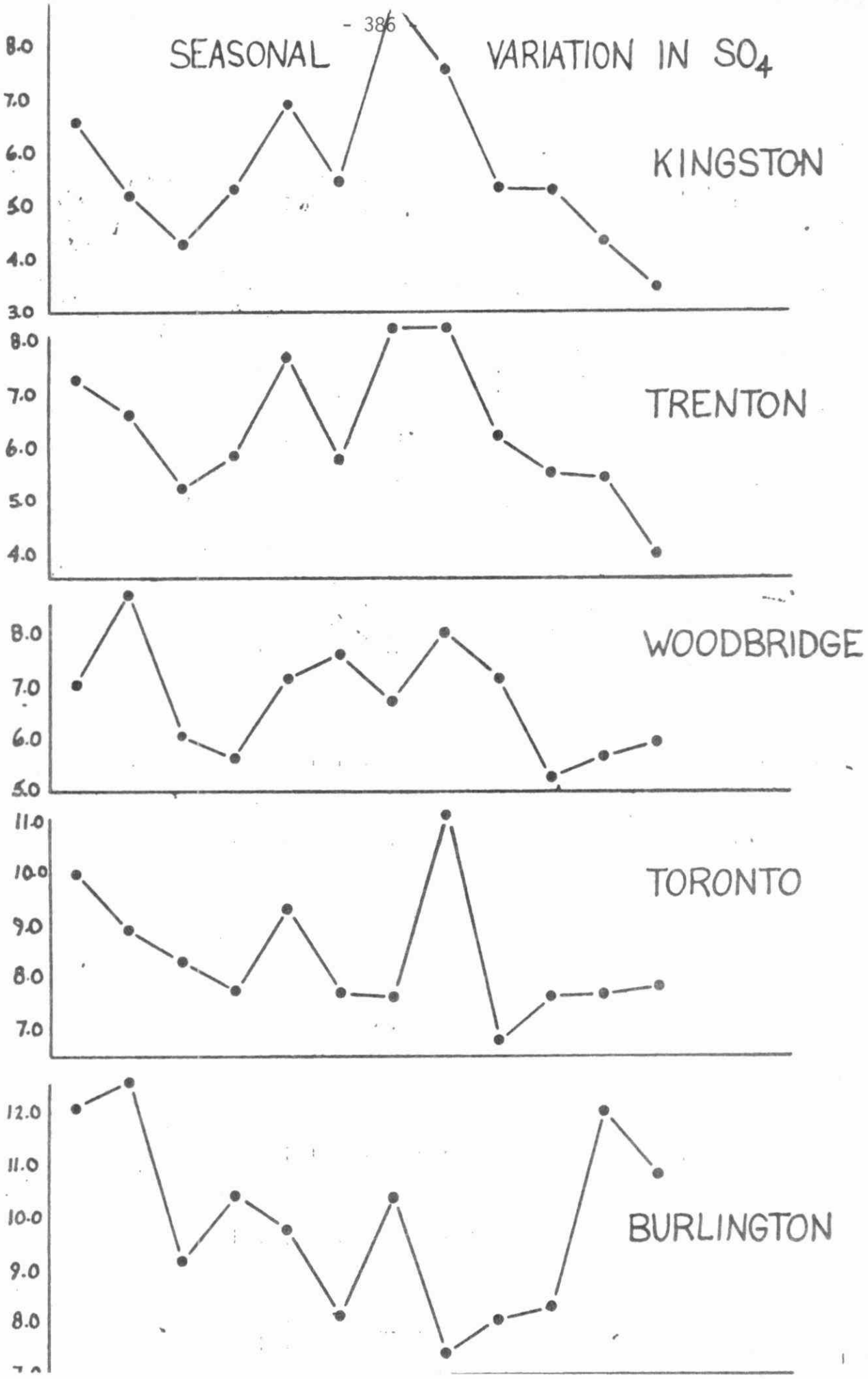



YEARLY VARIATION IN pH
KINGSTON
TRENTON
WOODBRIDGE
TORONTO
BURLINGTON
7.0
6.0
5.0
4.0
3.0
72
73
74
75
76
77


SEASONAL VARIATION IN NO_3
1.2
1.0
0.8
0.6
KINGSTON
1.8
1.6
1.4
1.2
1.0
0.8
TRENTON
1.4
1.2
1.0
0.8
WOODBRIDGE
1.8
1.6
1.4
1.2
1.0
TORONTO
2.0
1.8
1.6
1.4
1.2
1.0
0.8
BURLINGTON

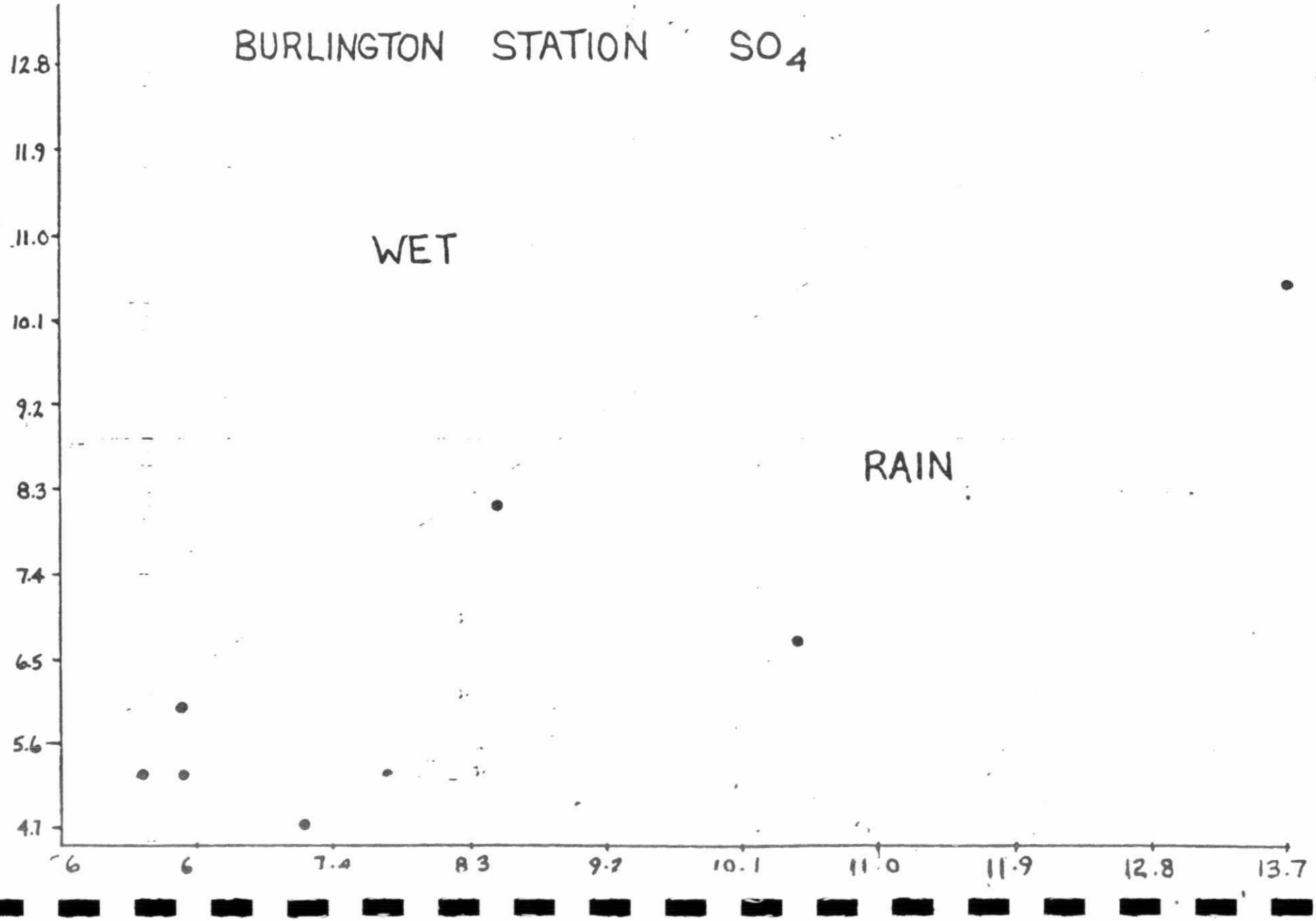
YEARLY VARIATION IN NO_3

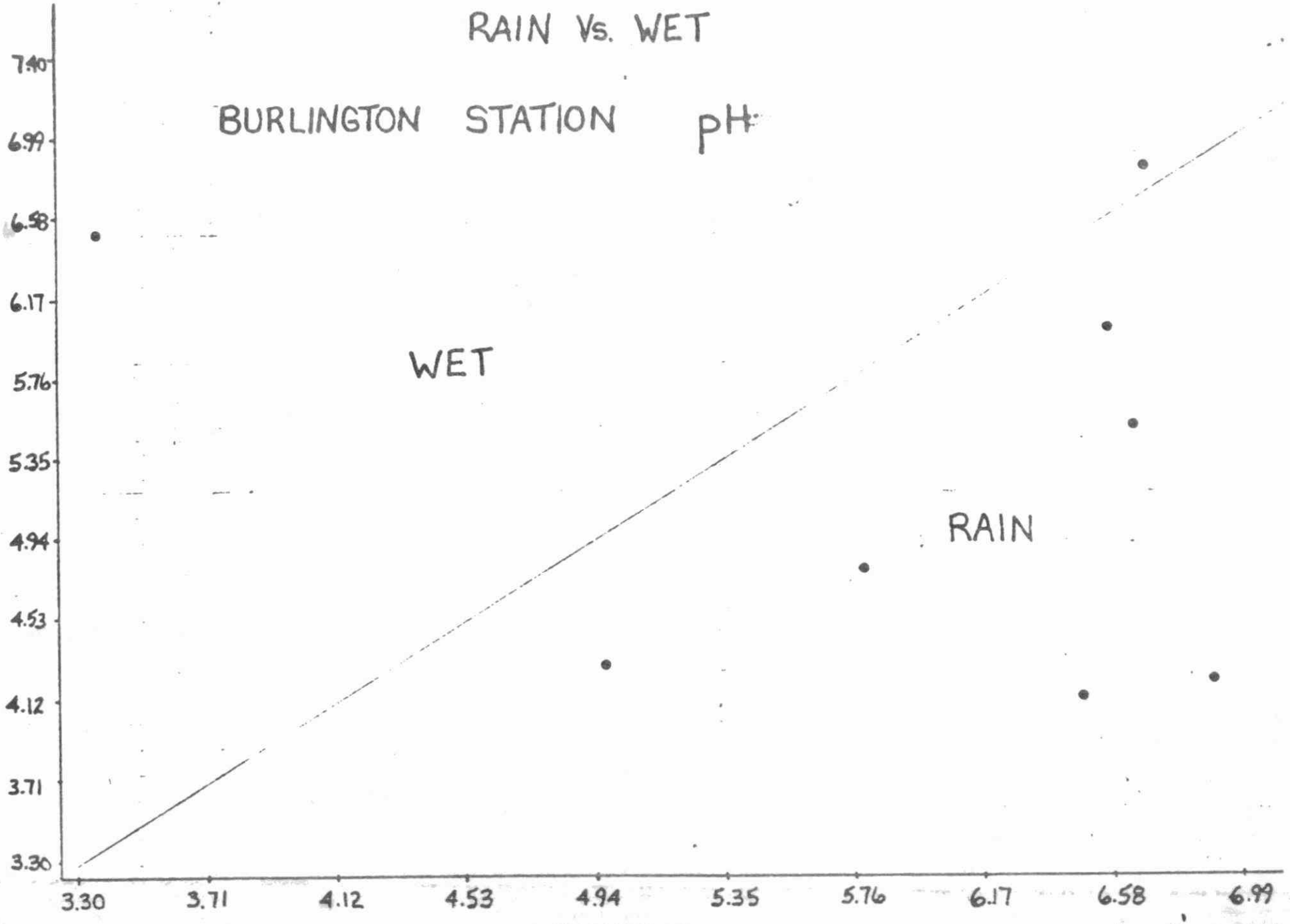



SEASONAL VARIATION IN SO_4
KINGSTON
8.0
7.0
6.0
5.0
4.0
3.0
TRENTON
8.0
7.0
6.0
5.0
4.0
WOODBRIDGE
8.0
7.0
6.0
5.0
TORONTO
11.0
10.0
9.0
8.0
7.0
BURLINGTON
12.0
11.0
10.0
9.0
8.0

RAIN Vs. WET

BURLINGTON STATION SO_4




RAIN Vs. WET
BURLINGTON STATION pH
WET
RAIN
7.40
6.99
6.58
6.17
5.76
5.35
4.94
4.53
4.12
3.71
3.30
3.30
3.71
4.12
4.53
4.94
5.35
5.76
6.17
6.58
6.99

APPENDIX FOURTEEN

ALKALINITY METHODOLOGY AS RELATED TO SOFT-WATER MEASUREMENTS

Serge Villard

DEFINITION OF ALKALINITY

THE ALKALINITY OF A WATER IS ITS QUANTITATIVE C PACITY TO NEUTRALIZE A STRONG ACID TO A DESIGNATED PH. THE MEASURED VALUE MAY VARY SIGNIFICANTLY WITH THE END POINT PH USED IN THE DETERMINATION. ALKALINITY IS A MEASURE OF A GROSS PROPERTY OF WATER AND CAN BE INTERPRETED IN TERMS OF SPECIFIC SUBSTANCES ONLY WHEN THE CHEMICAL COMPOSITION OF THE SAMPLE IS KNOWN.

USES IN ACID PRECIPITATION STUDY

- DELINEATE LAKES SUSCEPTIBLE TO ACIDIFICATION.
- ASSESS TRENDS IN ALKALINITY IN SPECIFIC WATER BODIES.
- CALIBRATE MODELS OF SPECIFIC WATERSHEDS.

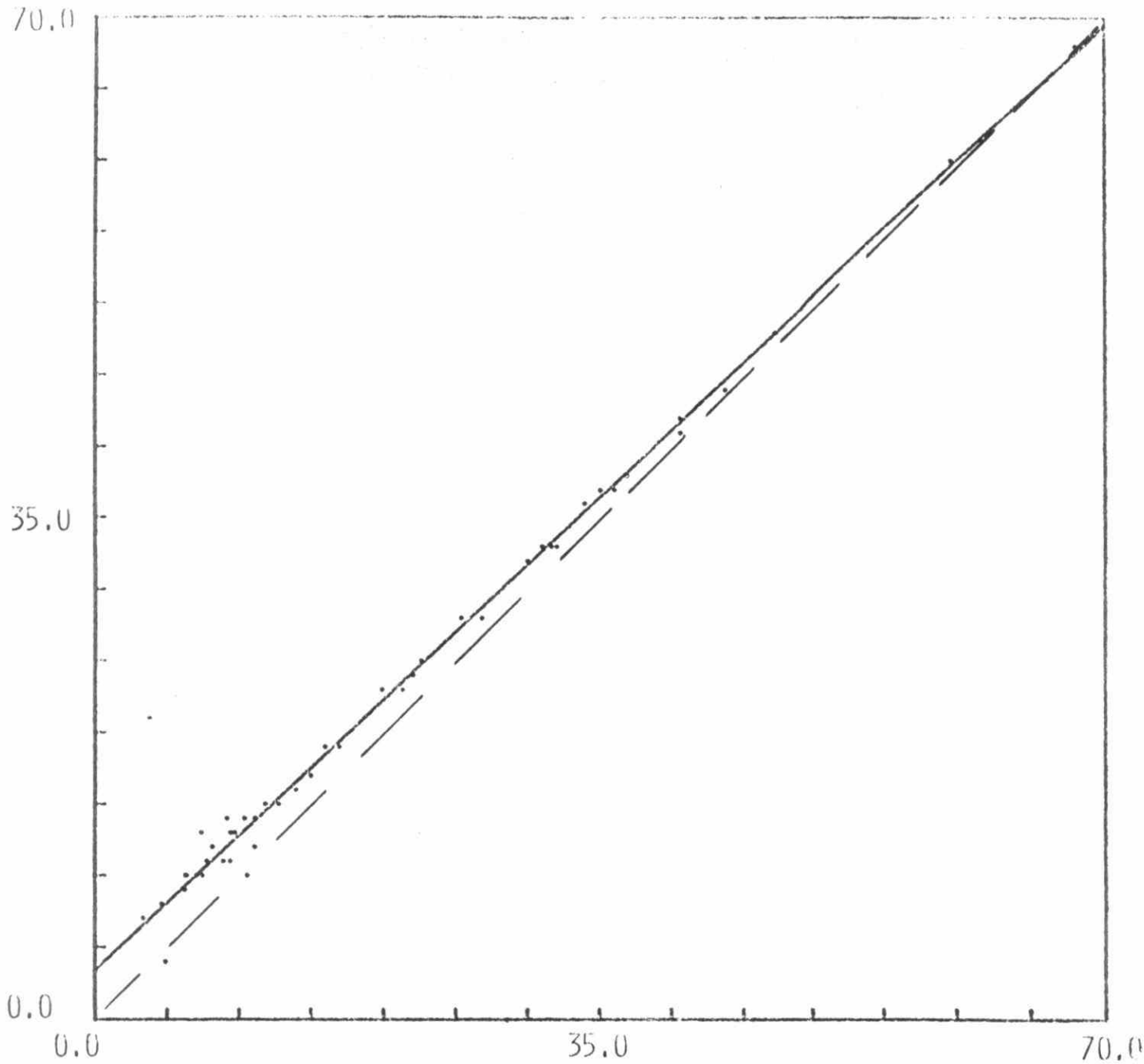
MINISTRY OF ENVIRONMENT (ONTARIO)
METHODOLOGY FOR ALKALINITY MEASUREMENT

PAST TO 1974 TOTAL FIXED ENDPOINT (TFE)
FISHER SEMIAUTOMATED TITRALYZER
ANALYTICAL RANGE 0 - 800 PPM $CaCO_3$
STANDARD DEVIATION 1.41 MG/L $CaCO_3$
ANALYTICAL MODE TOTAL FIXED ENDPOINT 4.5 (TFE).

1974 TO 1977 TOTAL FIXED ENDPOINT (TFE)
RADIOMETER ATS-1 AUTOMATED TITRALYZER
ANALYTICAL RANGE 0 - 250 PPM $CaCO_3$
STANDARD DEVIATION .40 MG/L $CaCO_3$
ANALYTICAL MODE TOTAL FIXED ENDPOINT 4.5 (TFE).

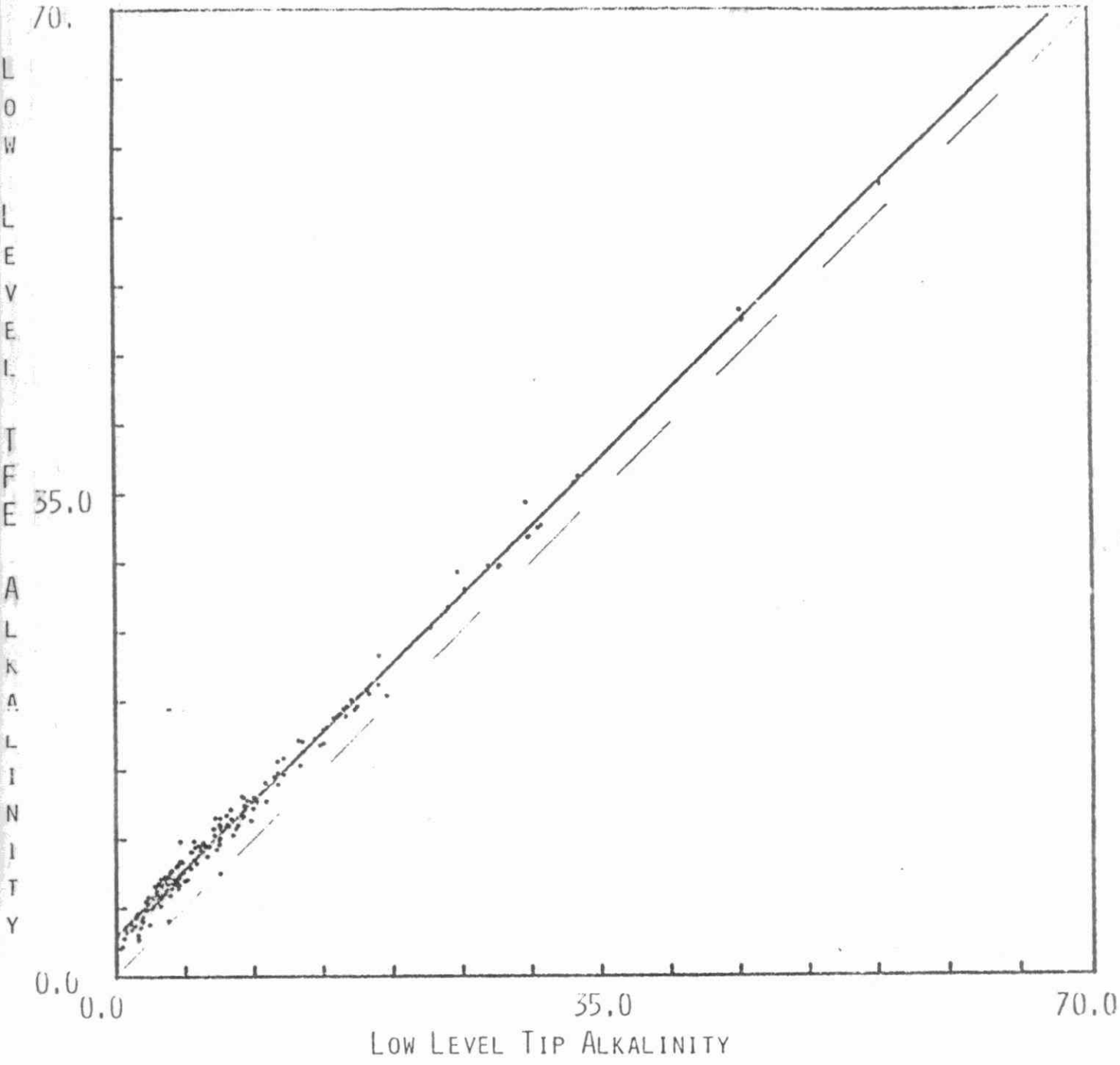
1977 - LIMITED USE TOTAL INFLECTION POINT (TIP)
MANUAL GRAN PLOT
RADIOMETER pH METER
STANDARD DEVIATION UNKNOWN - ESTIMATED 0.1 MG/L $CaCO_3$
ANALYTICAL MODE GRAN PLOT INTERPOLATION. TOTAL INFLECTION POINT (TIP).

1978 - ON SPECIFIC LAKES TOTAL INFLECTION POINT (TIP)
COMPUTERIZED GRAN PLOT AND DERIVATIVE
RADIOMETER pH METER
STANDARD DEVIATION 0.02 MG/L $CaCO_3$
ANALYTICAL MODE GRAN PLOT INTERPOLATION AND DIFFERENTIAL METHOD (TIP).



RELATIONSHIP BETWEEN LOW LEVEL
FISHER TOTAL FIXED ENDPOINT AND
TOTAL INFLECTION POINT ALKALINITY
ON MICROCOMPUTERIZED TITRATION SYSTEM.

UNITS IN MG/L $CaCO_3$



RELATIONSHIP BETWEEN LOW LEVEL
TOTAL FIXED ENDPOINT AND
TOTAL INFLECTION POINT ALKALINITY ON
MICROCOMPUTERIZED TITRATION SYSTEM

UNITS IN PPM $CaCO_3$

PERISHABILITY OF ALKALINITY PARAMETER

ACTUAL SAMPLE

ALL CONCENTRATION UNITS IN MG/L $CaCO_3$

CONTAINER TYPE / CONDITIONS	DAY 0	DAY 1	DAY 3	DAY 8	DAY 11
POLYSTYRENE / ROOM TEMP	7.20	7.21	7.87	8.66	9.12
PRINCE OF WALES SOFT GLASS / ROOM TEMP.		7.67	8.97	10.68	10.77

DISTILLED WATER

Initial Distilled Water Alkalinity	Polystyrene 10 Days Later	Prince of Wales (Soft Glass) 10 Days Later
.94 mg.L $CaCO_3$	.54 mg/L $CaCO_3$	4.95 mg/L $CaCO_3$

PERISHABILITY OF ALKALINITY PARAMETER

ACTUAL SAMPLES

PRINCE OF WALES (SOFT GLASS)

ALL CONCENTRATION UNITS IN MG/L $CaCO_3$

CONDITIONS	AFTER COLLECTION DAY 0	DAY 1	DAY 4	DAY 8	DAY 12
SAMPLE 1					
ROOM TEMP.	.67	1.02	3.25	3.50	
REFRIGERATED	.67	.81	1.50	1.93	
SAMPLE 2					
ROOM TEMP.	2.72	3.51	5.36	5.81	7.57
REFRIGERATED	2.72	2.84	3.63	4.25	4.82

PERISHABILITY OF ALKALINITY PARAMETER

ACTUAL SAMPLES

ALL CONCENTRATION UNITS IN MG/L $CaCO_3$

SAMPLES ALL STORED AT ROOM TEMPERATURE
IN 1 LITER PYREX GROUND
GLASS STOPPERED BOTTLES

SAMPLE	DAYS AFTER COLLECTION		
	2	3	14
1	3.87	3.73	3.38
2	1.78	1.50	1.48
3	1.64	1.42	1.44
4	2.94	2.85	2.96
5	2.55	2.43	1.87
6	2.20	2.11	1.88

CONCLUSIONS
PERISHABILITY STUDY

CONTAINER	CHANGE IN CONCENTRATION
PYREX	<.2 MG/L IN 14 DAYS. NOT REFRIGERATED
POLYSTYRENE	<.6 MG/L IN 4 DAYS. NOT REFRIGERATED
SOFT GLASS	NOT ACCEPTABLE >.5 - 1 MG/L IN 1 DAY. NOT REFRIGERATED REFRIGERATION SLOWS DOWN LEACHING FROM GLASS

THE PREDOMINANT CAUSE FOR CHANGE
SEEMS TO BE THE CONTAINER
AND NOT BIOLOGICAL ACTIVITY

COMPARISON OF ALKALINITIES CALCULATED BY THE GRAN AND DIFFERENTIAL METHODS

Lake	Initial pH	End Point pH		Calculated Alkalinity	
		Gran	Diff'l	Gran	Diff'l
Trout - composite	6.61	5.50	5.31	3.36	3.73
Basswood - composite	7.05	5.55	5.33	3.80	4.12
Black - composite	7.19	5.34	5.26	8.05	8.29
Black - surface	7.25	5.36	5.24	8.13	8.46
Fairy - epilimnion	7.04	5.41	5.35	4.96	5.09
Fairy - metalimnion	6.68	5.44	5.31	4.56	4.87
Fairy - hypolimnion	6.27	5.45	5.24	3.10	3.62
Penn - epilimnion	7.20	5.43	5.28	8.04	8.41
Penn(P1)-metalimnion	6.62	5.39	5.18	7.62	8.24
Penn(P2)-metalimnion	6.54	5.33	5.15	8.10	8.68

COMPARISON OF FIELD AND LABORATORY MEASUREMENTS

GRAN INFLECTION METHOD

UNITS MG/L $CaCO_3$

		GRAN CORRELATION	FIELD ANALYSIS CREW	GRAN CORRELATION	M.O.E. FIELD LABORATORY
GROUP A	LOUISA LAKE				
	1 METER	-	1.44	.999	0.90
	3 METER	-	0.51	.999	0.87
	5 METER	-	0.36	.999	0.85
	7 METER	-	0.72	.999	1.13
	SMOKE LAKE				
	1 METER	.999	2.79	.999	2.72
	3 METER	.997	2.38	1.000	2.78
	5 METER	.999	2.54	.999	3.06
	7 METER	.998	2.48	.994	3.07
GROUP B	KAWIGAMOG	-	6.12	.999	6.32
	BIG CEDAR	-	81.8	.999	85.7
	BUZZARD	-	5.42	.999	6.06
GROUP C	BIGWIND	.997	2.06	.999	2.49
	BRADY	.984	*2.55	.999	3.83
	CROSSON	.996	1.16	.999	0.65
	MOUNTAIN	.994	DATA DELETED		

STANDARD DEVIATION .30 MG/L $CaCO_3$
WITHOUT OUTLIER

STANDARD DEVIATION .48 MG/L $CaCO_3$
WITH OUTLIER

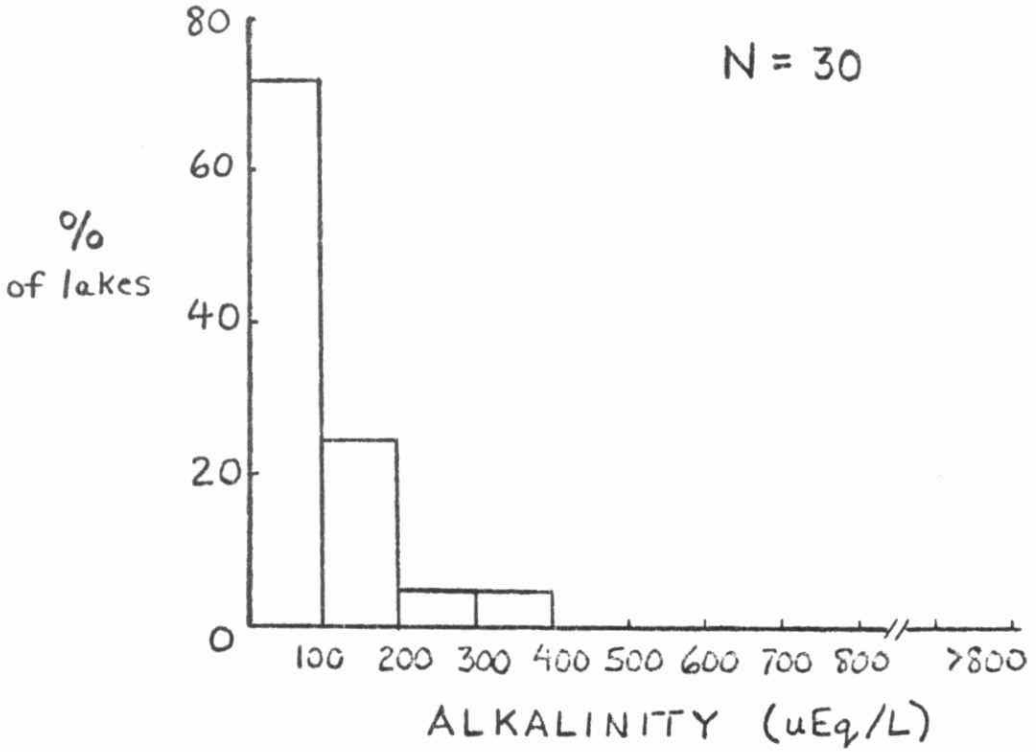
APPENDIX FIFTEEN

PRELIMINARY RESULTS OF LAKE SUSCEPTIBILITY SURVEYS

John Allin

Figure One

WATERSHED 2EA
GEORGIAN BAY



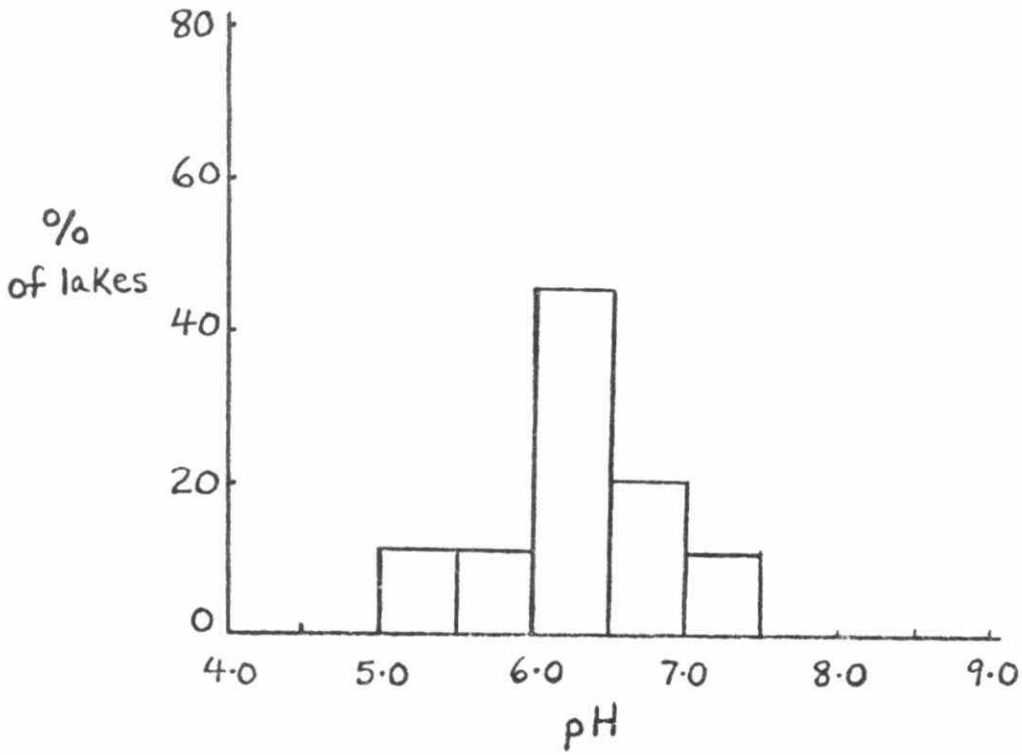
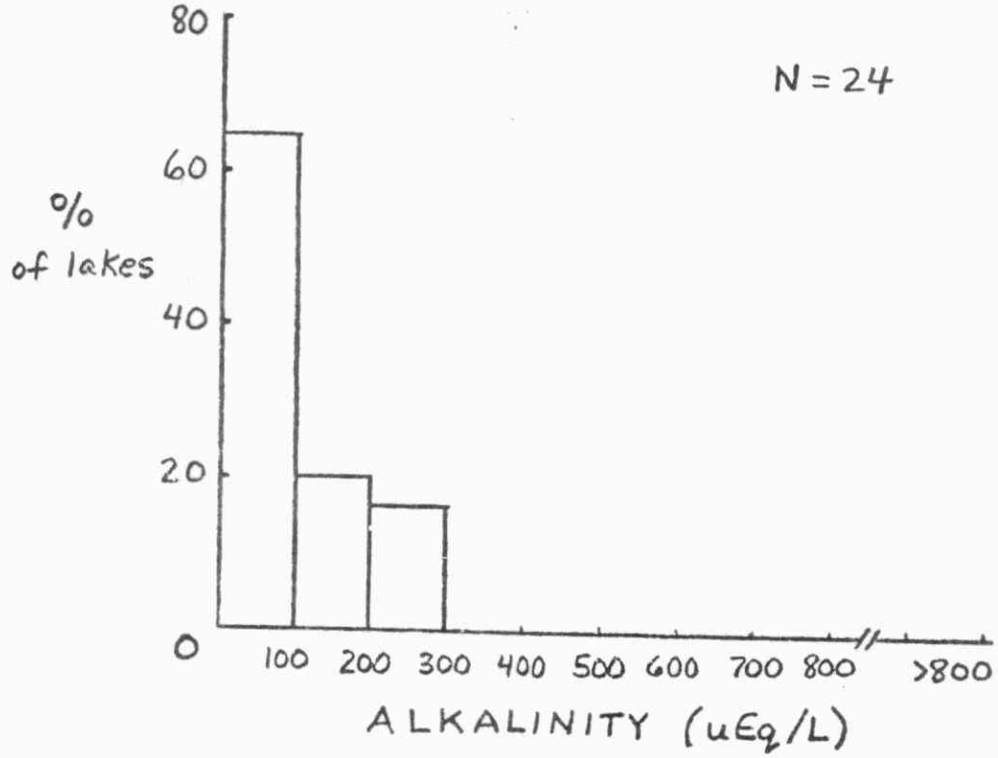


Figure Two

WATERSHED 2DC
STURGEON RIVER



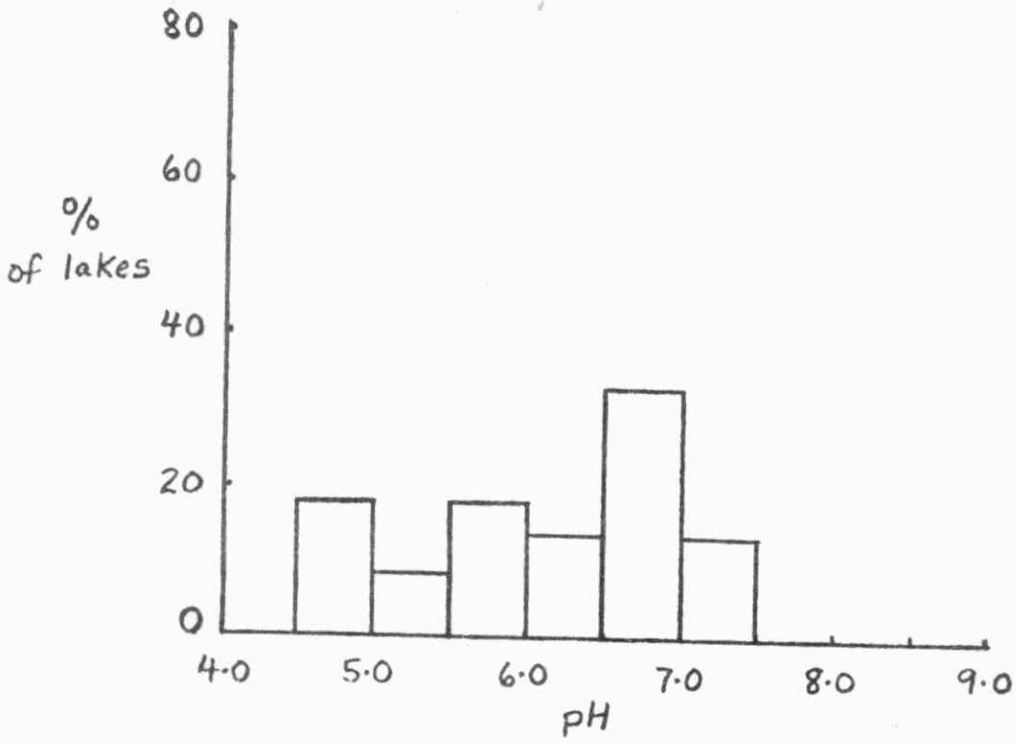
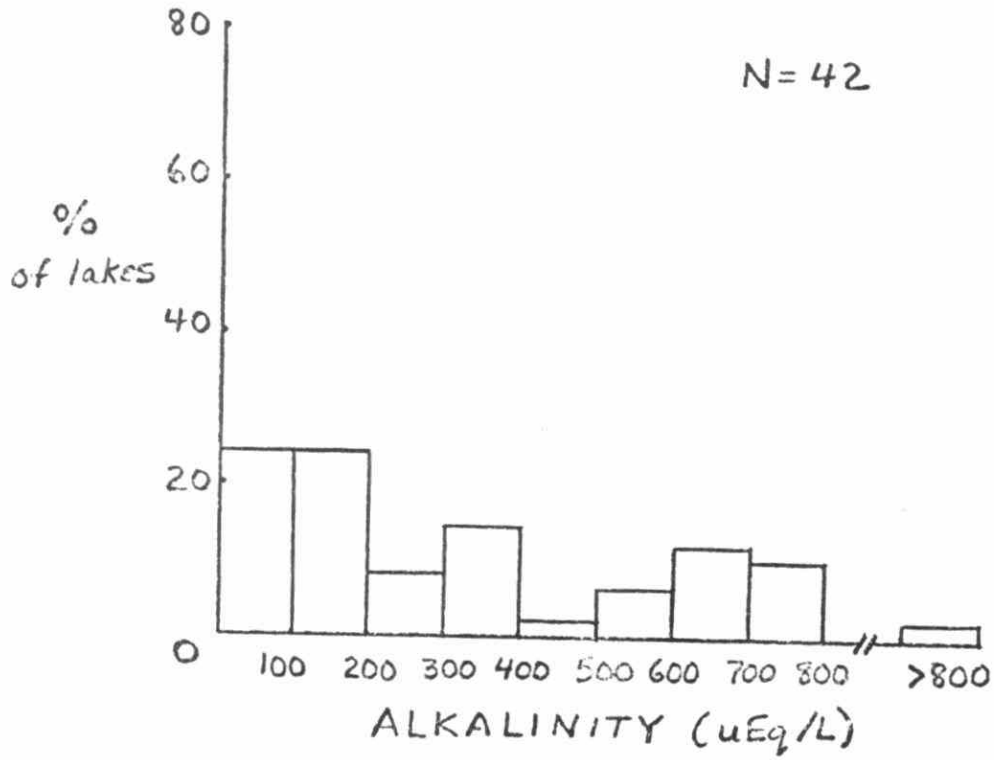
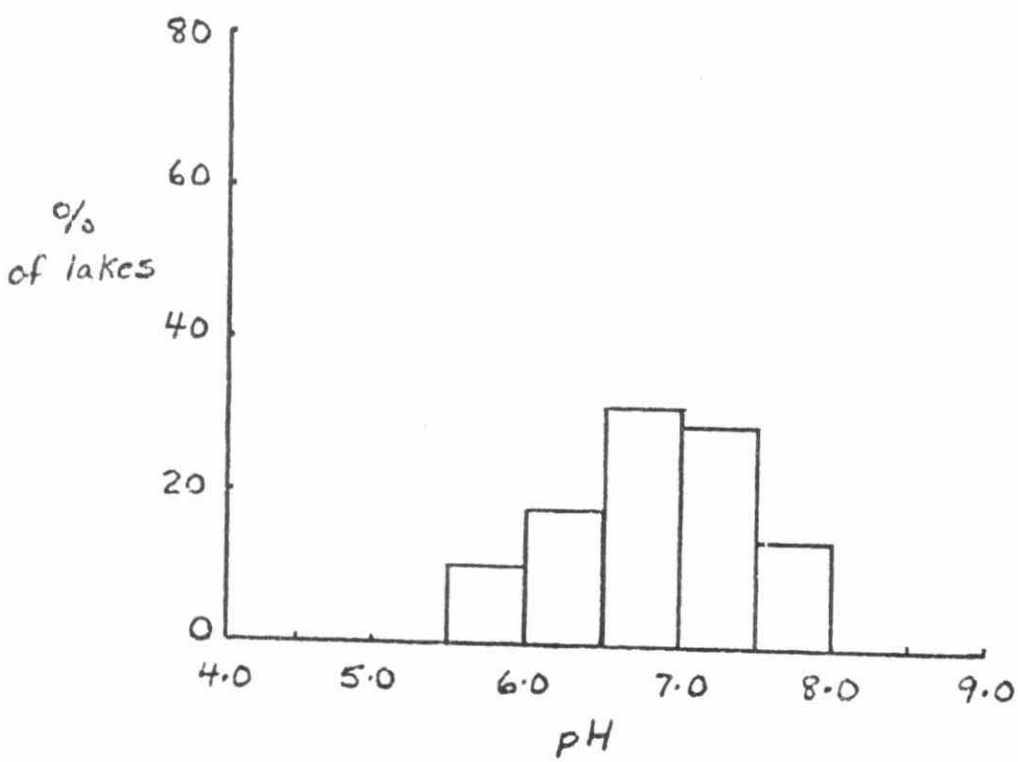


Figure Three

WATERSHED 2HF
CAMERON LAKE





At Sundridge last year, we proposed, and basically found acceptance for, a watershed program to be based where suitable but likely in North Central Ontario. Current major continuing study areas are Dillon's South-central Ontario program in the Muskoka-Haliburton area and the work from the Freshwater Institute in the Experimental Lakes Area. In North-central Ontario two major programs and a number of related interests originating from Sault Ste. Marie are being married into an Algoma watershed study. A study of persistent contaminants in an oligotrophic bay of L. Superior met with a program dealing with terrestrial influences upon water and hit it off. These two programs have evolved, along with the interest of others, into an Algoma program which in the broadest sense will examine the effects of "acid-rain" and other atmospheric contamination upon terrestrial and aquatic ecosystems.

A very strong terrestrial component is therefore part of the program. Ian will be describing that part shortly. Obviously at the heart of the problem is site selection, and it is one we have struggled with for some time now. Ontario has a considerable range in acid loading, contaminant loading, bedrock, soil, forest conditions and aquatic biotic assemblages. The two existing study areas can represent only a limited combination of these variables.

Some background is already available with which to see the differences in loading. I must admit that I am not the best choice to put some of these things together. But, from what I know, there appears to be rain with lowest pH's over the northeastern States with a general increase in pH from East to West in Ontario. This frequency diagram roughly represents what we see in precipitation in Algoma.

The values above 4.8 are a convenience and include a few values of over 5 plus a few where pH values are suspect. Generally, there are no direct sources. Sault Ste. Marie is 88 km distant and Wawa is some 150 km away. The data is

supported by event measurements made this summer where pH values fell between 3.96 and 4.72 from early June to last week with most values between pH 4.2 and 4.4. I gather these levels are close to what Peter is seeing in the Muskoka-Haliburtons but below what is apparently common in N-W Ontario.

Canadian situation - McBean paper at Air Quality Criteria Workshop.

Central Ontario - Dillon et al., MOE report.

I have not used recently available information but several published studies allow a partial overview of Ontario's aquatic resources.

First, Ryder (1964) looked at TDS and alkalinity in waters of Ontario and found them to vary according to glacial history. In spite of difficulties in determining alkalinity, the most poorly buffered systems were found to stretch in a band across Ontario. The apparent extent of poorly buffered systems is considerably less than one would expect only from bedrock geology but it is known that other basin features exert considerable influence. However, if Ryder's isopleths for lowest alkalinity is transposed to Olver & Martins (1976) lake trout lake distributions then, easily, 80% of known lake trout producing systems are in the areas of lowest buffering. The lake trout distributions are well described by Martin and Olver but they form a belt of varying width extending from East to West. Johnson et al., (1977), for the Percis symposium related several limnological characteristics of lakes to associations of walleye, northern pike, lake trout and small mouth bass. Their broader analysis also indicates that lake trout are particularly important (this is an excerpt from their Table 4 of only districts falling within Ryder's poorly buffered area) but also we see intrusions from the north of assemblages with

walleye, and from the south of assemblages with small mouth bass, both valued species.

Narrowing it down, closer to home, the MNR lake inventory system provides a good data set. There are lakes in that data set having low pH and low conductivity although both characteristics have a considerable range. These lakes (approx. 50) range in size from 5 ha to about 850 with most between 50 and 150 ha. In order to establish a perspective for the watershed we would ultimately work on, we began, this year, a survey of lakes. Ours ranged in size from about 30 to 150 ha with most lakes between 30 and 125 ha (slightly narrower range than MNR). The conductivities we found were generally similar to that found by MNR with about 50% of lakes from both data sets having conductivities <30 µmhos. The pH's were somewhat different, however. We revisited some of the lakes done by MNR and found that their data for a limited set of 12 lakes followed the same rank order of pH from high to low but their pH's were generally higher, most likely because they used a near surface grab sample. Generally, the pH's we found were lower (lowest 5.0) with about 25% having pH's <6.0.

These lakes are almost all trout lakes and range throughout the district. The assemblages other than "trout only" described by Johnson et al. are few. Although it's fuzzy, it's apparent that although lake trout are common, the majority of lakes with known populations are brook trout (13) lakes. This results in part from the nature of preferred systems by the species - lake trout, from Martin and Olver, tend to be more successful in the larger, deeper lakes - and the generally smaller, shallower nature of systems in the Algoma area. Also, the distribution is influenced by stocking policy. Brook trout are more popular.

From what is known, the Algoma watershed is typical of the size and chemistry of lakes in the watershed. Although

I won't say much about the chemistry - Floyd will do that - or the basin - Ian will do that - pH in the system progresses from less than 5 in the headwater lake to about 6.5 in the lower lakes. Conductivity ranges from between 5 and 10 in the headwater lakes to about 50 in the lower lakes.

In the uppermost lake, we were unable to catch fish of any sort. In the second lake, white suckers and brook trout are present but there are few age classes of either species. In the lowest two lakes, brook trout, lake trout, common white sucker and burbot are present. Both salmonid species in all lakes are self-sustaining although hatchery fish have been added to both lower lakes over the year. The second lake from the headwater has a population that is obviously troubled.

Ministry of Natural Resources
Ontario

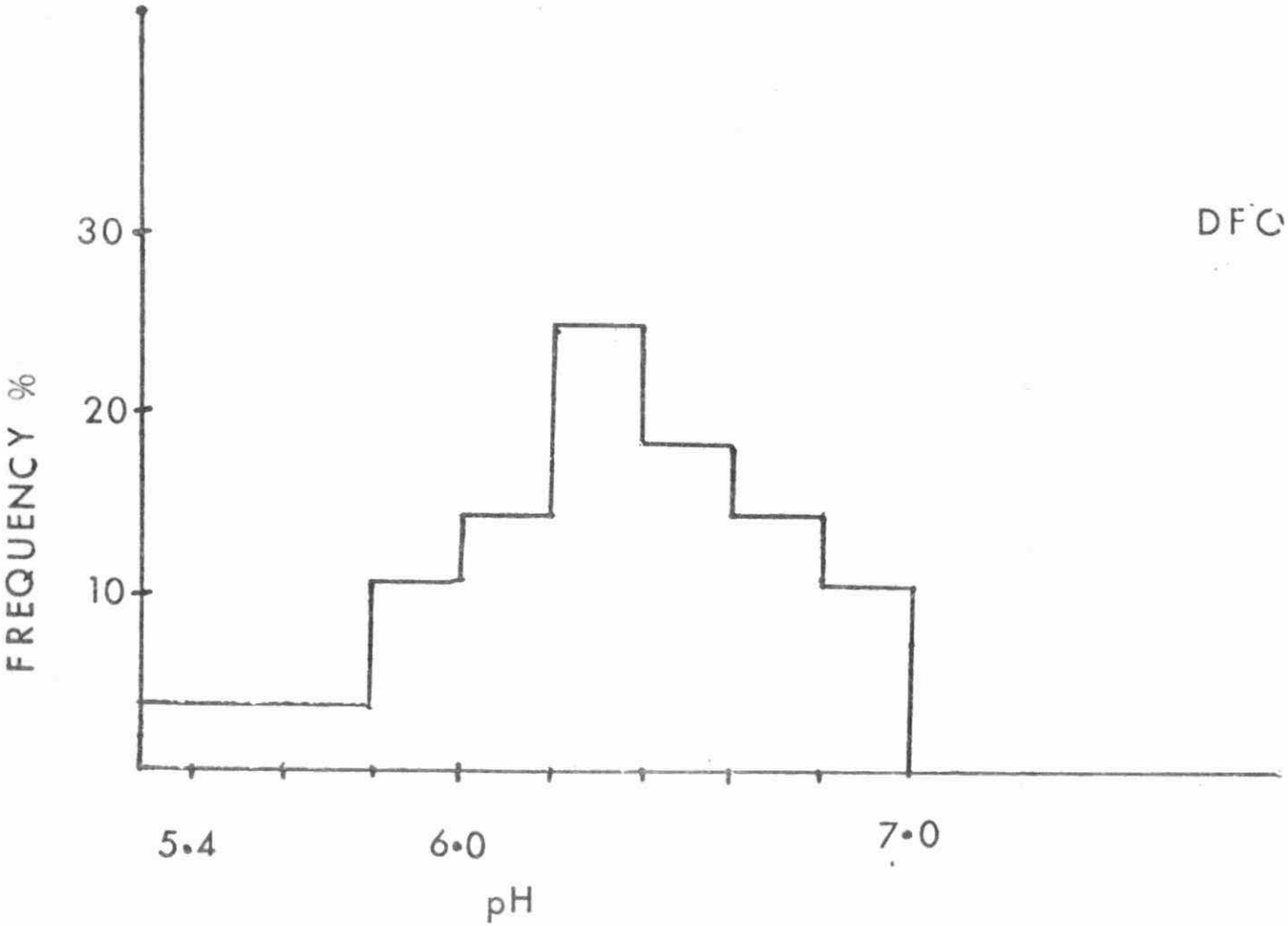
SAULT STE. MARIE
ADMINISTRATIVE DISTRICT
NORTHEASTERN REGION

Legend
MAP 21

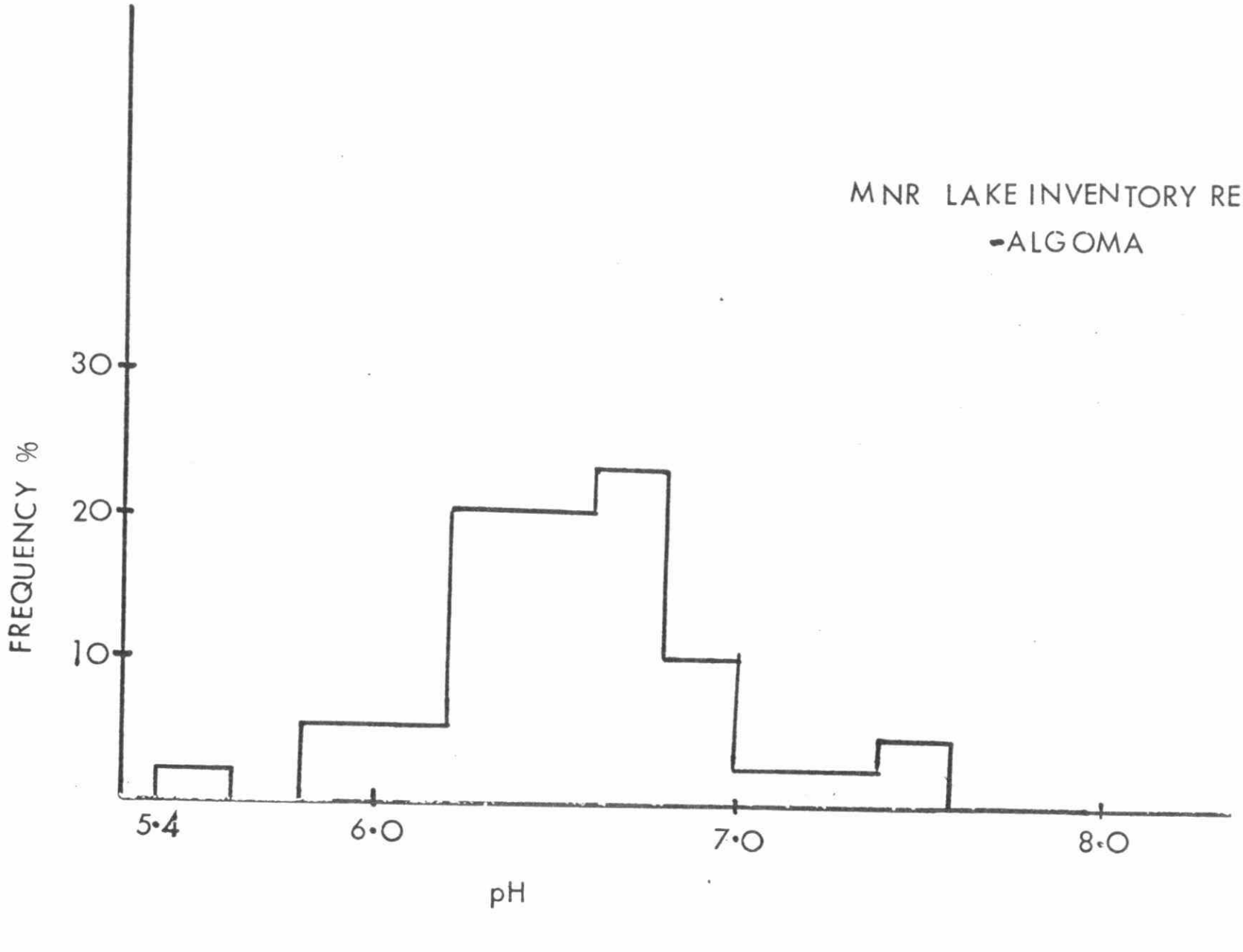
SPORTS FISHERIES

- L Lake Trout
- B Brook Trout
- R Rainbow Trout
- P Pickerel, Pike
- O Rainbow Spawning Streams

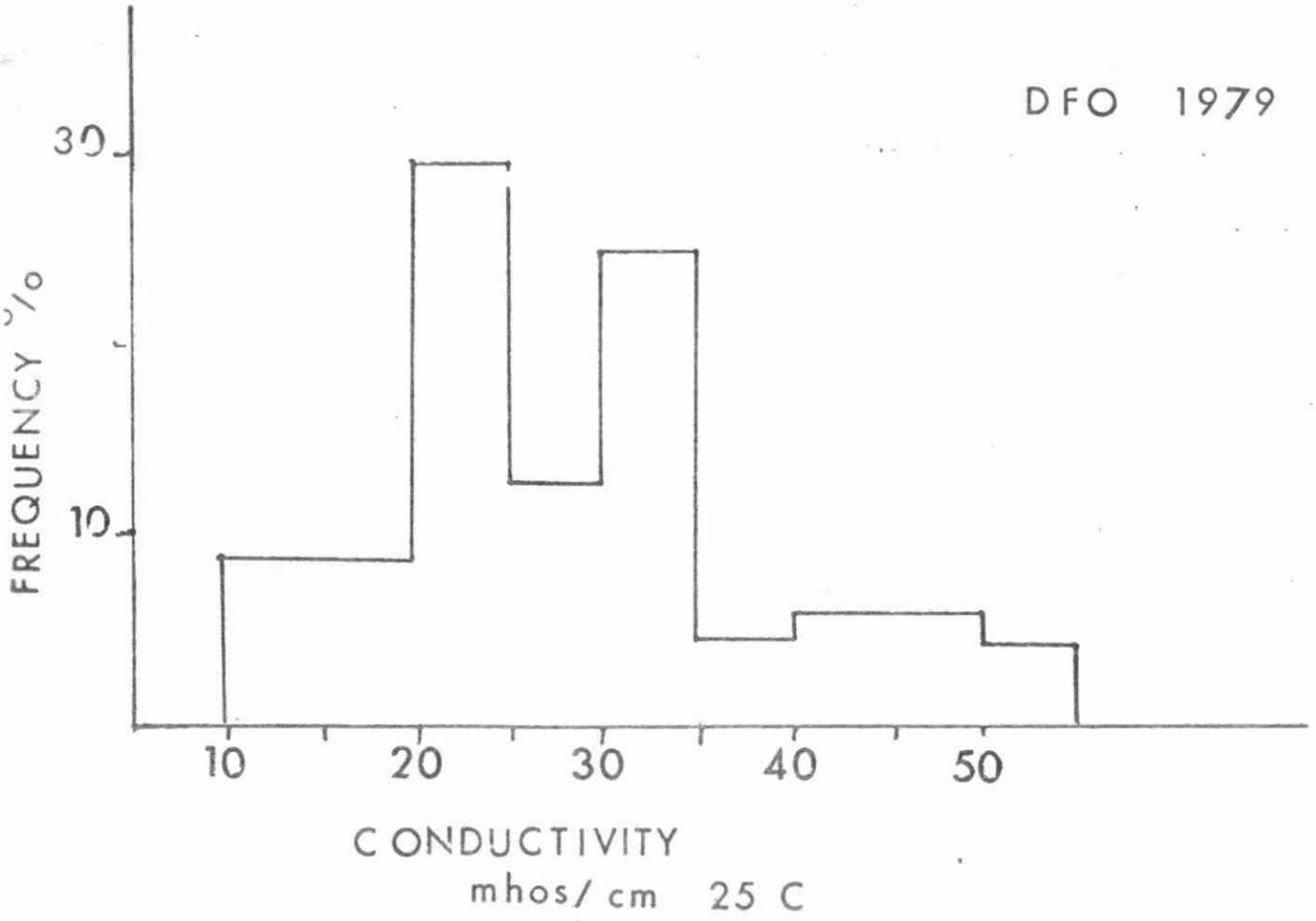
Source: MNR Div. of Fish and Wildlife
Date: Sept. 1978

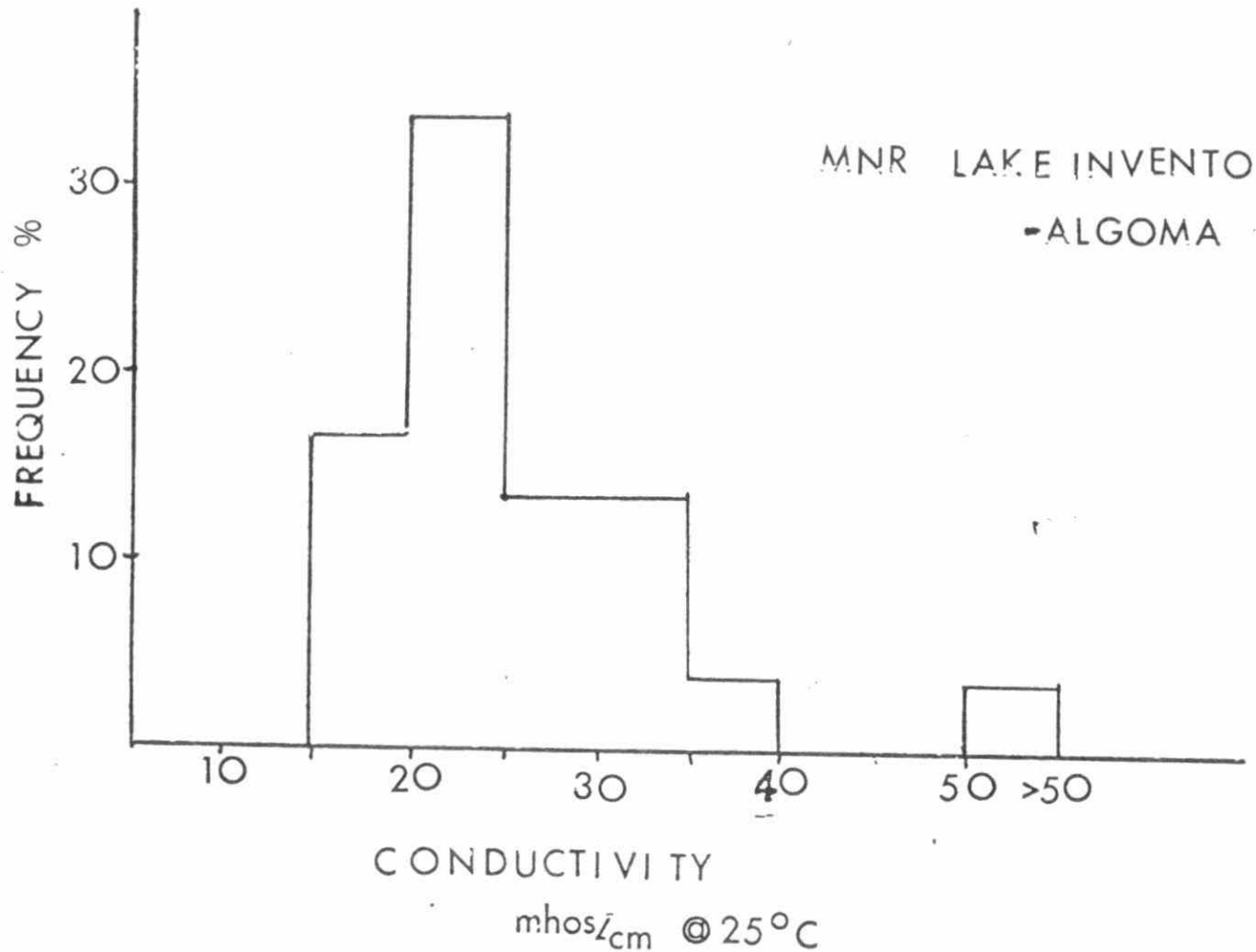


DFO 1979


MNR LAKE INVENTORY RECORDS
-ALGOMA
FREQUENCY %
30
20
10
5·4
6·0
7·0
8·0
pH

DFO 1979




MNR LAKE INVENTORY RECORDS
-ALGOMA
FREQUENCY %
30
20
10
10
20
30
40
50
>50
CONDUCTIVITY
mhos/cm @ 25°C

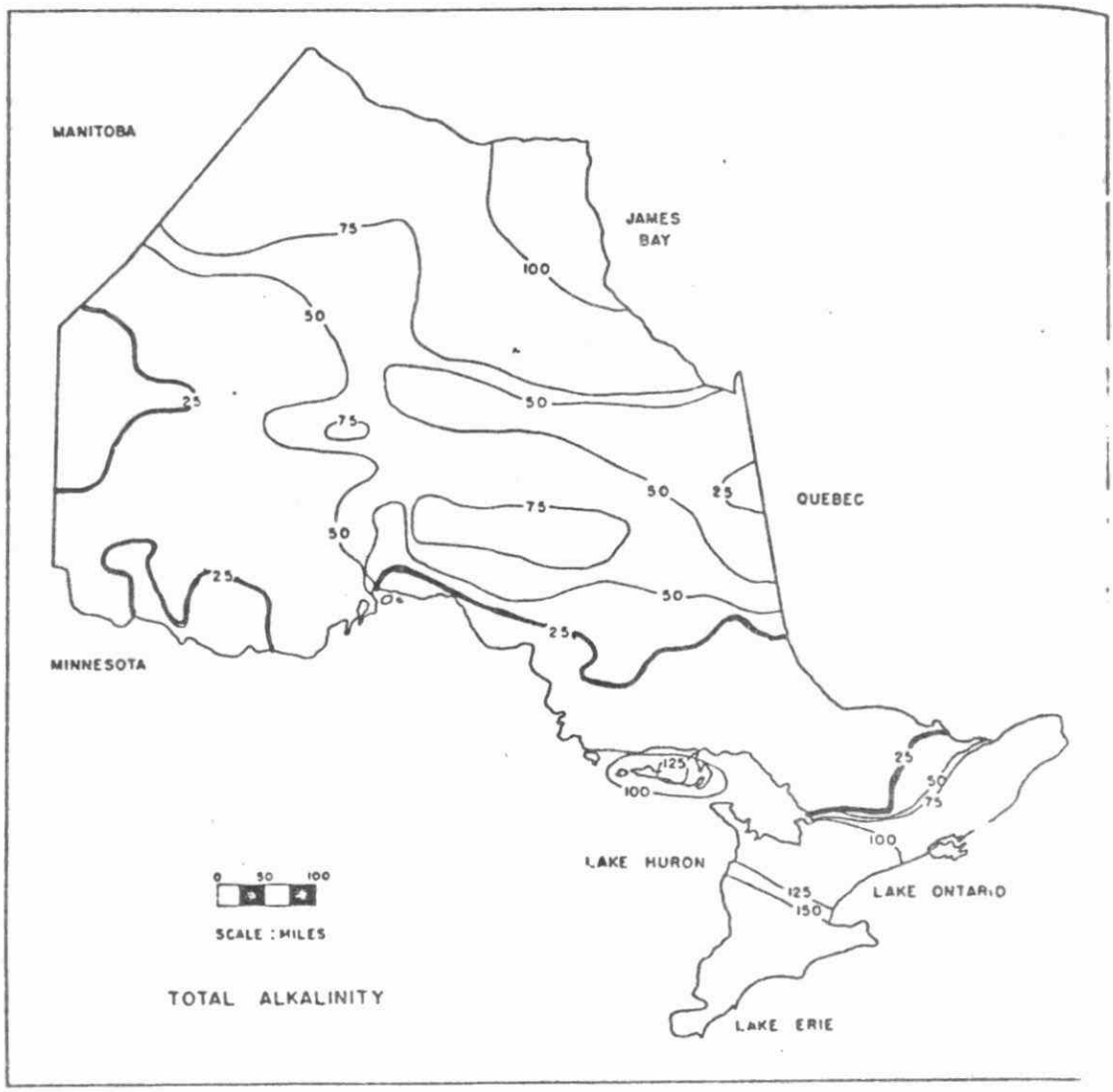
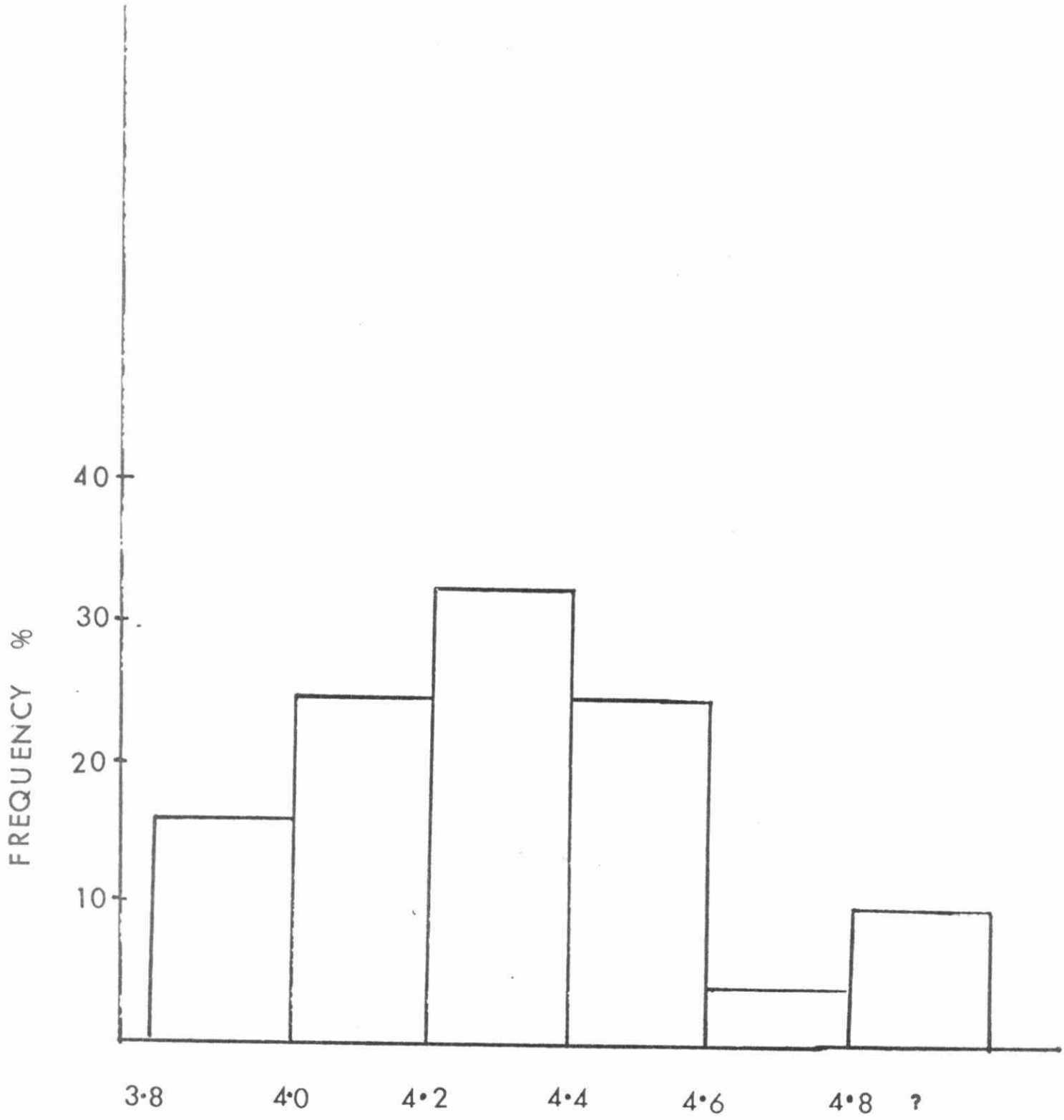


FIGURE 7.—Isopleth map of mean concentrations of total alkalinity (p.p.m.) based on data from 31[illegible] Ontario lakes.



BULK pH, 1976, 77, part of 79, Batchawana Bay

1

Ministry of Natural Resources

SAULT STE. MARIE
ADMINISTRATIVE DISTRICT
NORTHEASTERN REGION

From Johnson et al.(1977)

District	No. Lakes	LB	L	LWP	LWPB	LP	LPB	B	P	PB	W	WP	WPB	WB
Kenora	98	+	+	+	+	+	+	-	11	+	-	26	28	+
Fort Frances	65	-	+	15	+	12	+	-	12	-	-	40	+	-
Atikokan	111	-	+	17	+	11	+	+	14	+	+	26	12	+
Terrace Bay	53	+	11	-	-	+	-	-	25	-	+	51	-	-
White River	44	-	+	+	-	+	-	-	14	-	-	75	-	-
Wawa	51	-	39	+	-	+	-	-	10	-	+	29	-	-
Sault Ste. Marie	65	12	71	-	-	-	-	+	+	-	+	-	+	+
Blind River	77	+	66	-	+	+	+	+	+	+	-	-	-	-
Sudbury	45	+	+	-	+	+	+	+	27	20	+	+	13	-
North Bay	45	+	22	-	16	+	+	+	+	+	+	+	16	13
Espanola	45	+	29	-	+	+	+	16	+	+	-	-	16	-
Algonquin Park	126	17	67	-	-	-	-	13	-	+	-	-	-	-
Pembroke	47	13	+	-	+	+	-	23	19	+	+	-	17	+
Parry Sound	91	20	+	+	+	-	+	25	+	+	+	+	19	+
Bracebridge	135	20	22	-	-	-	-	44	-	+	+	-	+	+
Bancroft	86	29	+	-	-	+	+	42	+	+	+	+	+	+
Minden	97	30	20	-	-	-	-	38	-	-	+	-	-	10

5

APPENDIX SEVENTEEN

CHEMISTRY OF TURKEY LAKE BASIN

Floyd Elder

Figure One

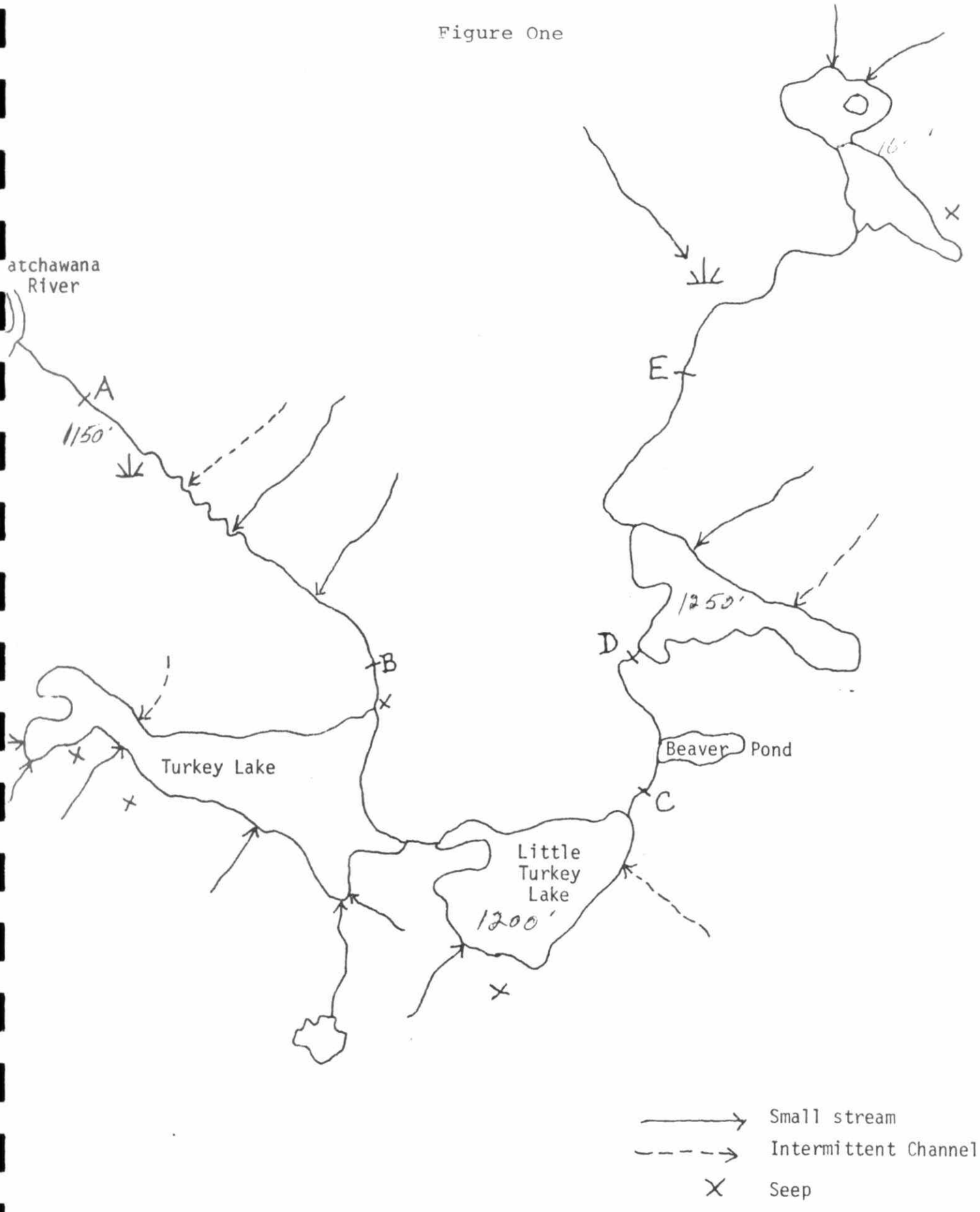

atchawana River
A
1150'
B
Turkey Lake
E
1250'
D
Beaver Pond
C
Little Turkey Lake
1200'
Small stream
Intermittent Channel
Seep

Figure Two

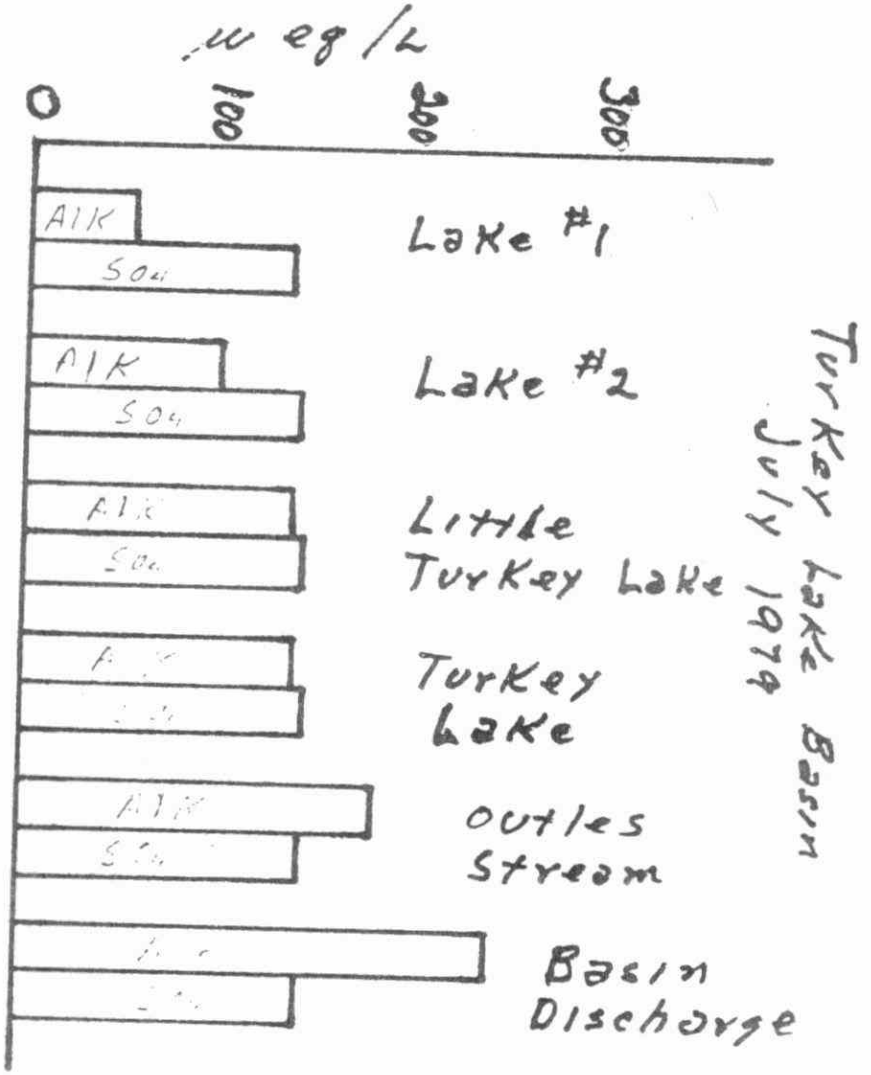
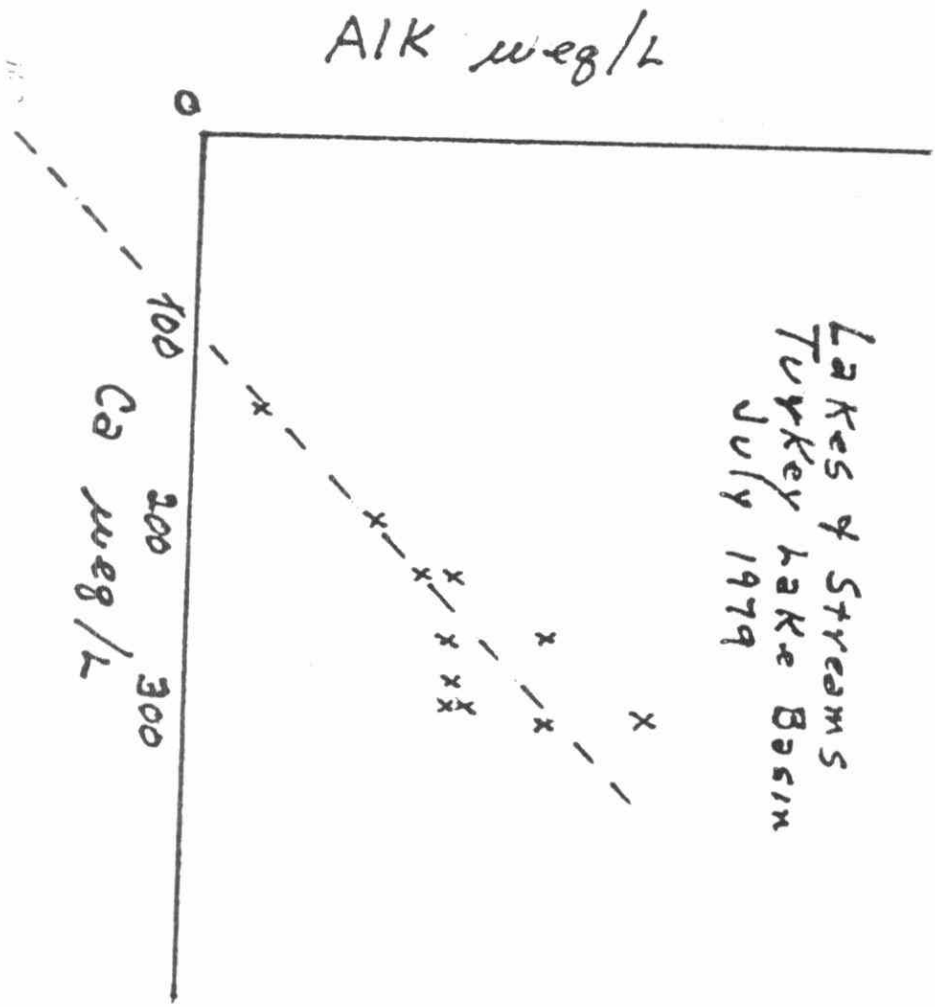

μ eq/L
0
100
200
300
Alk
SO4
Lake #1
Alk
SO4
Lake #2
Alk
SO4
Little Turkey Lake
Alk
SO4
Turkey Lake
Alk
SO4
Outles Stream
Alk
SO4
Basin Discharge
Turkey Lake Basin
July 1979

Figure Three



APPENDIX EIGHTEEN

TERRESTRIAL ENVIRONMENT OF THE ALGOMA

WATERSHED STUDY

Ian Morrison

FOREST STANDS[1]

STAND	WORKING GROUP	AGE[2]	SITE	AREA (HA)
1	$\underline{wS}_3$ B_2 wB_2 sM_1 E_1 rO_1	89	1	8.4
2	$\underline{hM}_8$ wS_1 yB_1	154	2	106.4
3	$\underline{hM}_9$ yB_1	134	3	89.4
4	$\underline{hM}_7$ yB_2 wS_1	154	1	26.9
5	$\underline{hM}_9$ yB_1	139	2	31.1
6	$\underline{hM}_7$ yB_2 eC_1	135	2	26.5
7	$\underline{hM}_6$ yB_3 wS_1	144	2	9.9
8	$\underline{hM}_9$ wB_1	128	3	30.8
9	$\underline{yB}_5$ hM_4 wB_1	186	2	40.5
10	$\underline{hM}_{10}$	121	3	18.6
11	$\underline{hM}_5$ yB_3 eC_1 wB_1	114	3	29.3
12	$\underline{C}$ eC_6 wB_2 $6S_1$ B_1	183	3	23.6
13	$\underline{hM}_{10}$	121	3	49.9
14	$\underline{hM}_9$ yB_1	139	3	133.2
15	$\underline{hM}_9$ yB_1	154	1	184.4
16	$\underline{hM}_9$ yB_1	116	2	44.0
17	$\underline{yB}_5$ hM_5	149	2	4.0
18	$\underline{hM}_8$ yB_2	134	3	6.5
19	$\underline{hM}_7$ yB_2 wS_1	134	2	44.4
20	$\underline{hM}_5$ yB_3 wS_2	134	2	99.4
21	$\underline{hM}_8$ yB_2	134	3	37.2
22	$\underline{hM}_9$ yB_1	126	2	99.2
23	$\underline{hM}_{10}$	139	3	27.5
24	$\underline{hM}_3$ yB_2 wS_2 eC_2 B_1	134	3	1.3
25	$\underline{hM}_4$ yB_2 eC_2 B_1 wS_1	144	2	20.4
PROTECTION FOREST		-	4	86.9
OPEN WETLAND		-	-	18.2
FOREST AND WETLAND TOTAL		-		1,297.9

[1] FOREST RESOURCES INVENTORY DATA

[2] 1980 DATUM

SITE CLASS DISTRIBUTION

SITE CLASS	AREA (HA)	%
SITE CLASS 1	219.7	16.9
SITE CLASS 2	525.8	40.5
SITE CLASS 3	447.3	34.5
SITE CLASS 4	86.9	6.7
OPEN WETLAND	18.2	1.4
LAND TOTAL	1,297.9	100.0

- regardless of species

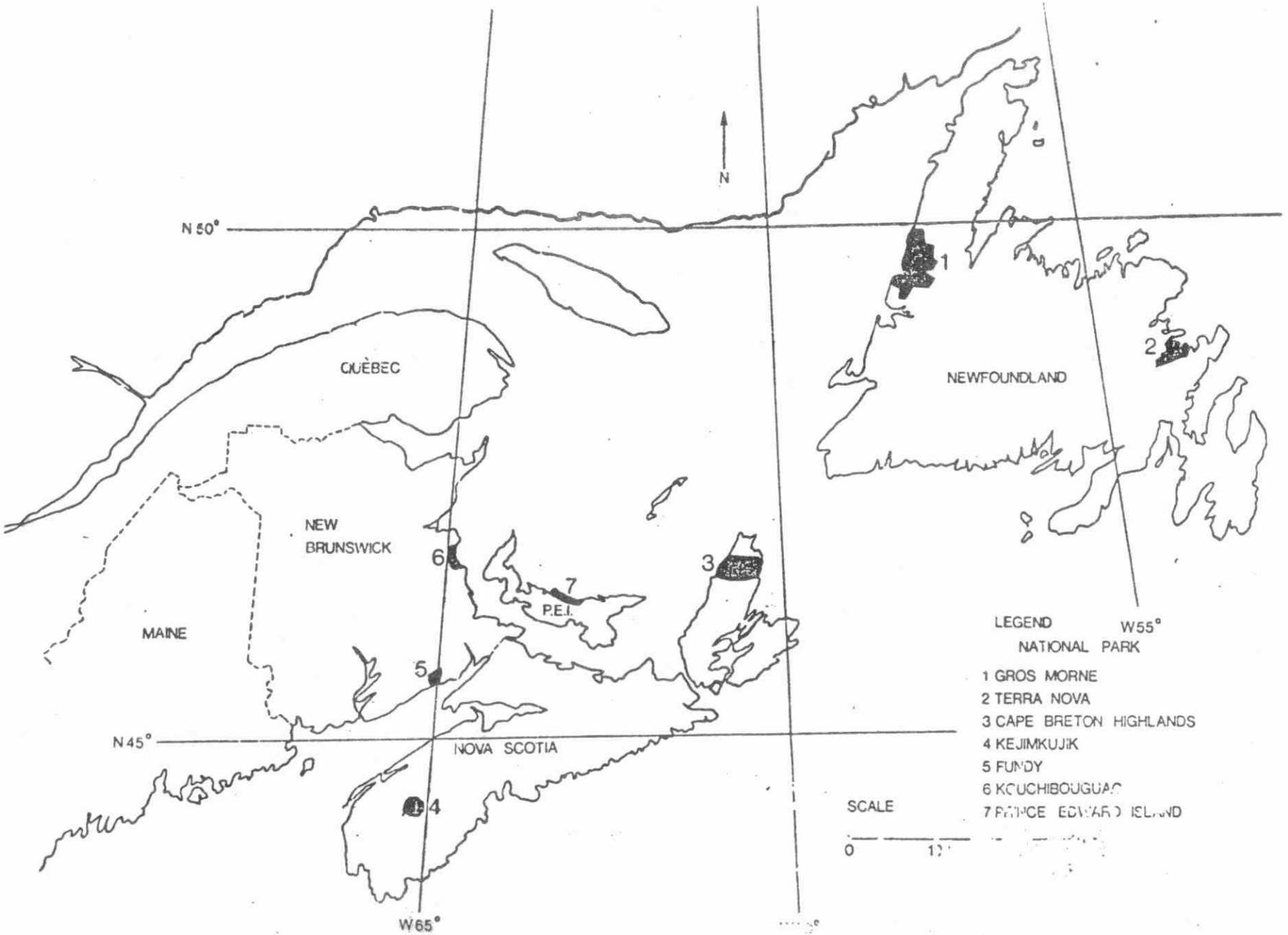
APPENDIX NINETEEN

ACID RAIN INVESTIGATIONS ON THREE LAKE BASINS IN KEJIMKUJIK NATIONAL PARK, N. S.

J. J. KEREKES

Canadian Wildlife Service, Atlantic Region

Three lake basins lying mainly on Devonian granite are investigated for the impact of acid rain. The lake waters are very soft (salinity $\approx$10 mg/l), oligotrophic (total phosphorus $\approx$8 mg/m^3), and the ionic composition reflects strong maritime influence ($Na > Mg > Ca > K$, $Cl > SO_4 \gg HCO_3$). Two lakes, Beaverskin (9.4 km^2, $\bar{z}$ = 2.2m) and Pebbleloggitch (0.33 km^2, $\bar{z}$ = 1.4m) are headwater lakes with small lake surface-drainage basin area ratios (1:2.5 and 1:4.8, respectively) while Kejimkujik (24 km^2, $\bar{z}$ = 4.4m) has a surface-drainage ratio of 1:28. The average moisture surplus is 0.8 m/yr and the flushing rates are 1, 2.9 and 5.5 times/yr respectively. The pH values are the lowest in winter but a sudden drop in pH was not observed in the last two springs because the snow did not accumulate during the relatively mild winters. The annual weighted mean value of pH of precipitation is 4.6 in 1978 (pH 4.2-5.1 monthly means). Pebbleloggitch (pH 4.2-4.6) has colored, humic water (110 Hazen U) and is showing signs of self-accelerated acidification due to the expansion of Sphagnum. Beaverskin (pH 5.0-5.4) lacks peat deposits on its basin and its water is very clear (5 Hazen U). Kejimkujik is intermediate (pH 4.8-5.2, 80 Hazen U). All three lakes support fish populations and fish eating birds are present, but only stunted yellow perch is found in Pebbleloggitch Lake. Evidence is presented that pH levels dropped approximately 1.0 units in the area in the last 25 years.


N
N 50°
QUÉBEC
NEW BRUNSWICK
MAINE
NOVA SCOTIA
P.E.I.
NEWFOUNDLAND
N 45°
W65°
W55°
1
2
3
4
5
6
7
LEGEND
NATIONAL PARK
1 GROS MORNE
2 TERRA NOVA
3 CAPE BRETON HIGHLANDS
4 KEJIMKUJIK
5 FUNDY
6 KOUCHIBOUGUAC
7 PRINCE EDWARD ISLAND
SCALE
0

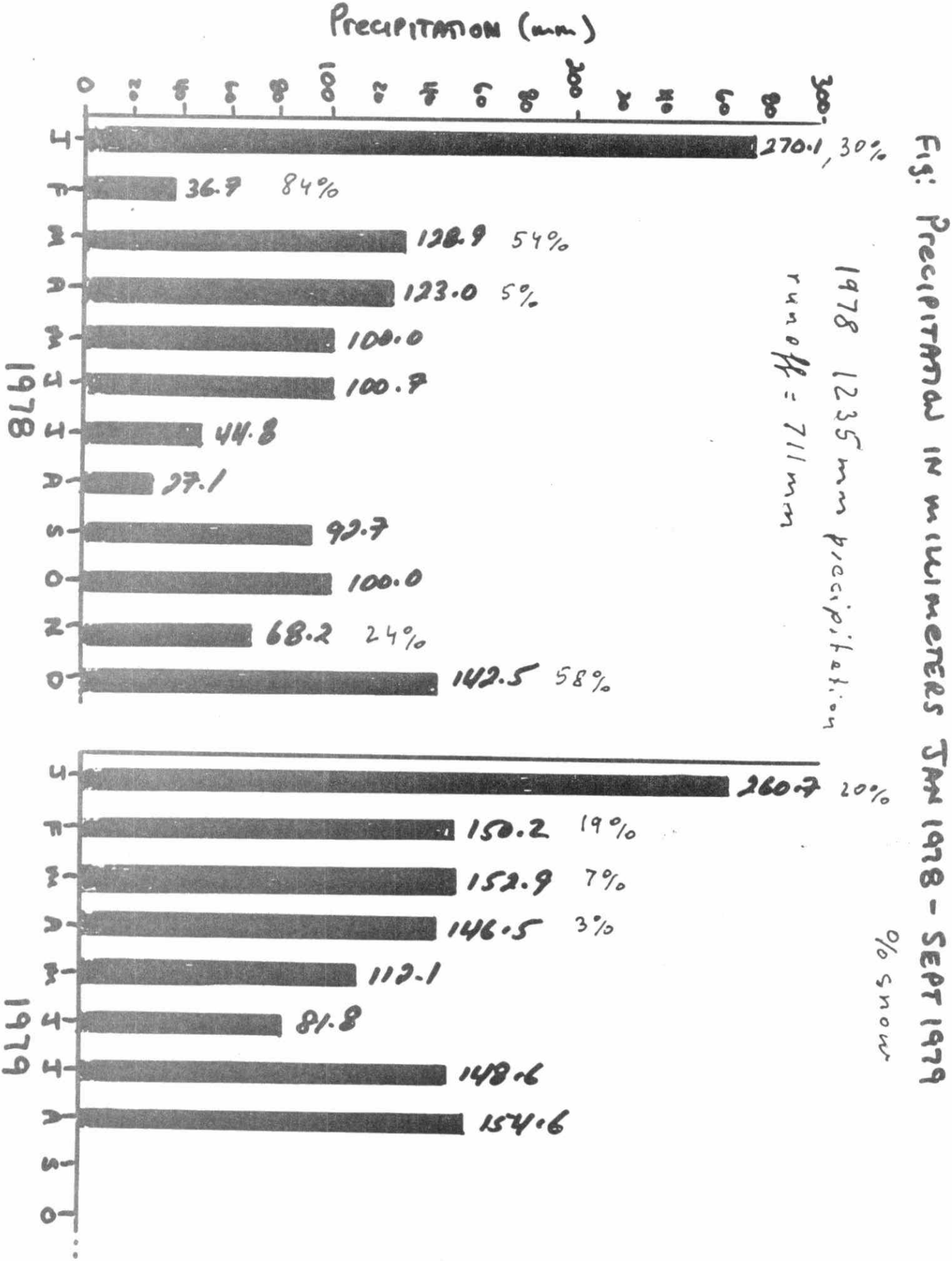
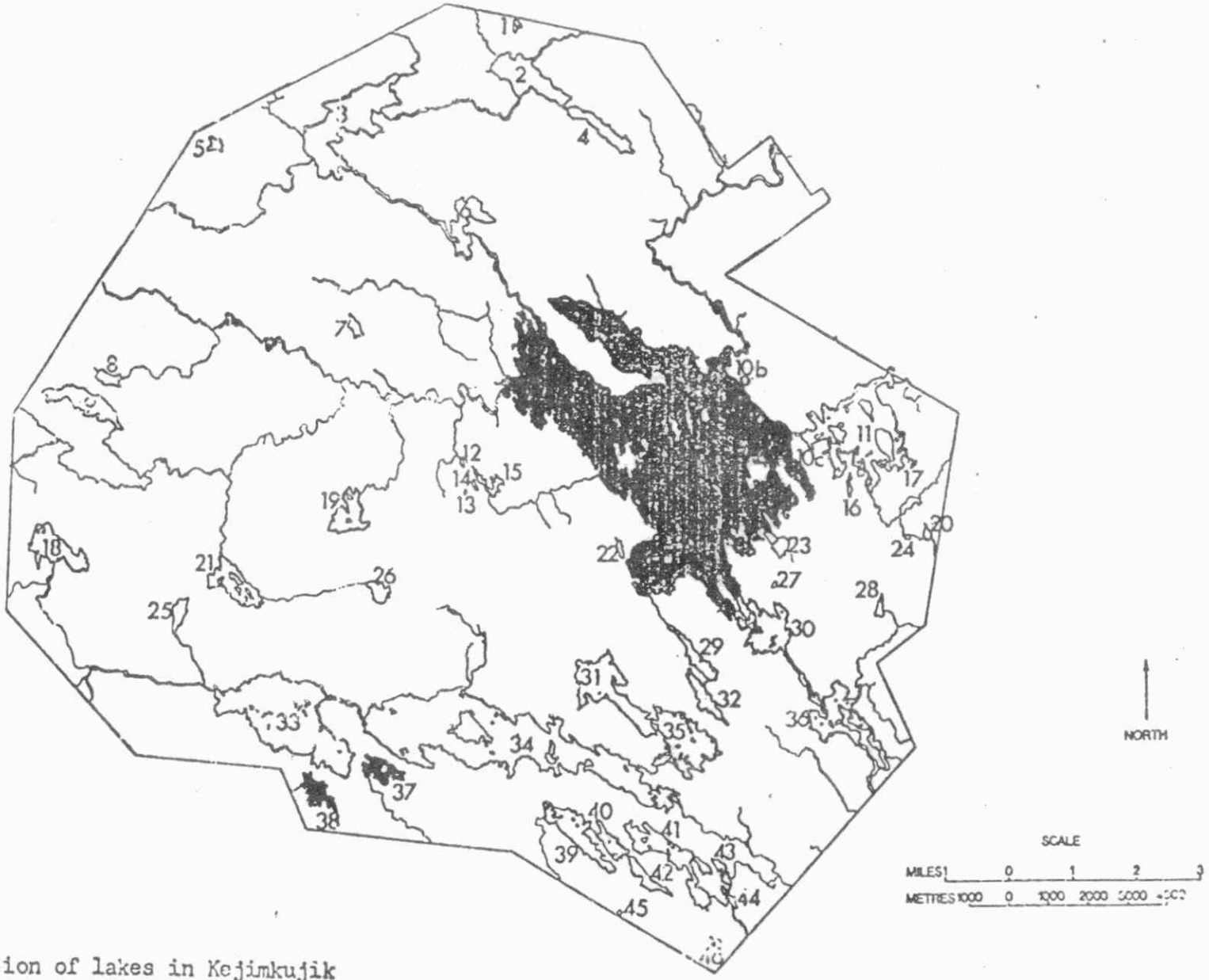


Fig: Precipitation in millimeters Jan 1978 - Sept 1979



Location of lakes in Kejimkujik National Park, N.S.

Lake	Area km^2	$\bar{z}$ m	Area / Drainage	Flushing 1/y	pH	Color Hazen U	Conductance µmho/cm
Beaverskin	0.4	2.2	1:2.5	1	4.9-5.6	5	23
Kejimkujik	24.3	4.4	1:25.0	5.5	4.8-5.2	80	30
Pebbleloggitch	0.33	1.4	1:4.8	3	4.1-4.5	110	34

Ionic dominence

Na > Mg > Ca > K , Cl > SO_4

Beaverskin lake water Aug, 1978

	µeq./l		
Na	113	Cl	127
Mg	33	SO_4	54
Ca	15		181
K	5		
H	5		
	171		

Kejimkujik lake water-

Na	122	Cl	150
Mg	56	SO_4	62
Ca	25		212
H	13		
K	5		
	228		

Table 3. The distribution of fishes in the lakes in Kejimkujik National Park.

Lake	Lake whitefish	Brown trout	Brook trout	Golden shiner	Creek chub	White sucker	Brown bullhead	American eel	Banded killifish	Ninespine stickleback	White perch	Yellow perch
Back			+	+		+	+	+	+		+	+
Beaverskin			+	+			+	+	+		+	+
Den												
Big Dam (East)		-	-	+		-	+	+			+	+
Big Dam (West)		-	+	-	-	+	+	+	-		+	+
Big Red												+
Central				-		+	+	+	+		+	+
Coblielle	-		+	-		+	+	+	-		+	+
* Dennis Boot												
Frozen Ocean			-			-	-	-			-	-
George				+		+	+	+			+	+
Grafton			+	+		+	+	-			+	+
High			+	+		+	+	-	+			+
Hilchemakaar			-	+		+	+	-	+		+	+
Kejimkujik	-	-	-	+	-	+	+	-	+	+	+	+
* Liberty												
* Little Liberty												
Little Peskowesk			+	+		+	+	-	+		+	+
Little Red												+
Loon				+		+	+	-	+		+	+
Lower Silver			+	-		+	+	-	+		+	+
Luxion			+									+
McGinty			+	+		+		-	+		+	+
Mountain	+		+			+	-	-			+	+
Mud			+			+	+	-				+
North Cranberry			+	+			+	-	+			+
Pebbleloggitch							+	-				+
Peskawa			-	+		+	+		+			+
Peskowesk	-		+	+		+	+	-	+	+		+
Poplar												

Mersey River

• 1954/58 $\bar{x}$ = 5.9 range 5.4 – 6.5

□ 1978
$\bar{x}$ = 5.00
range = 4.7 – 5.2

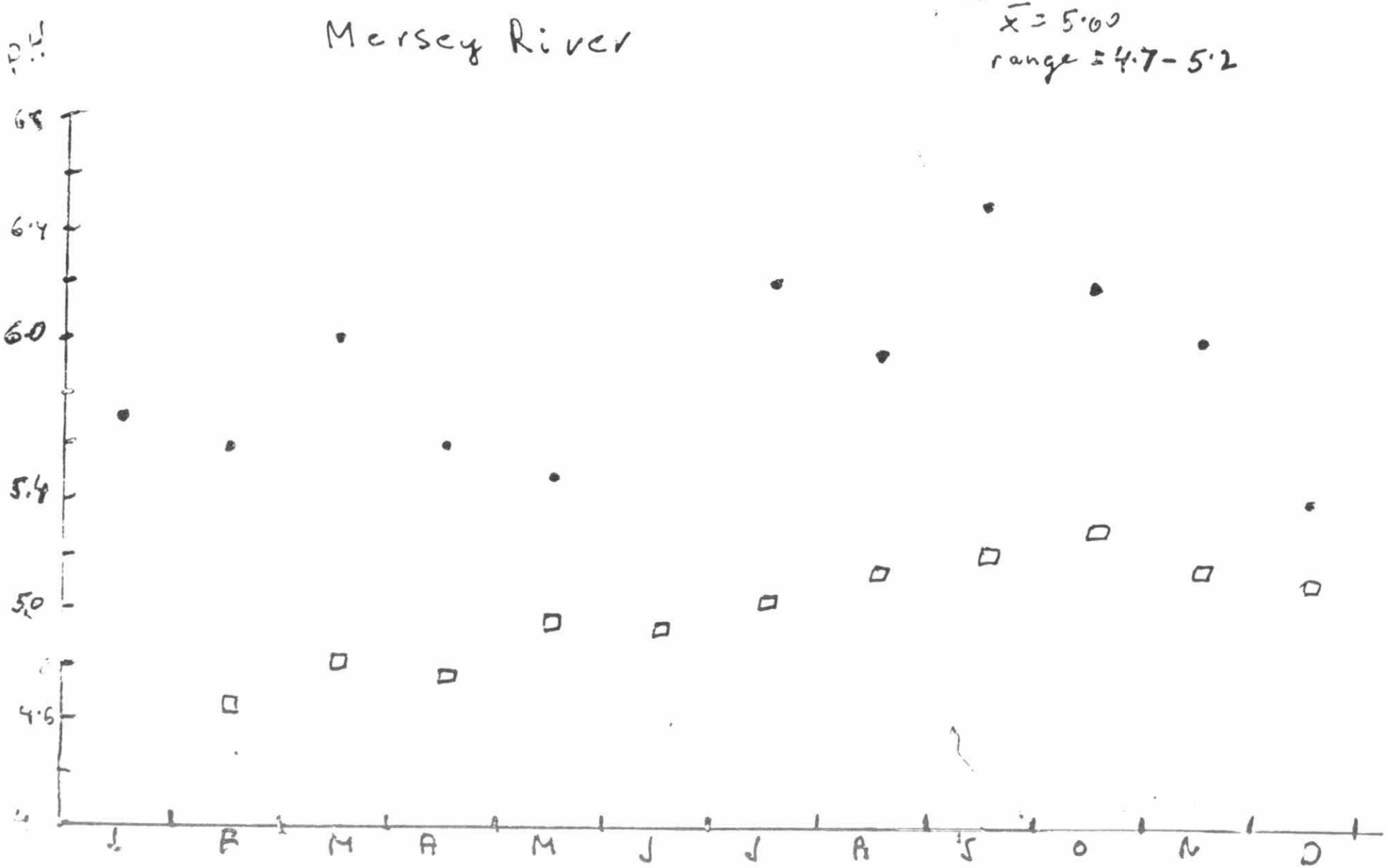


Fig: Lower Mersey River pH, Feb 78 - Sept 79 (lab values)

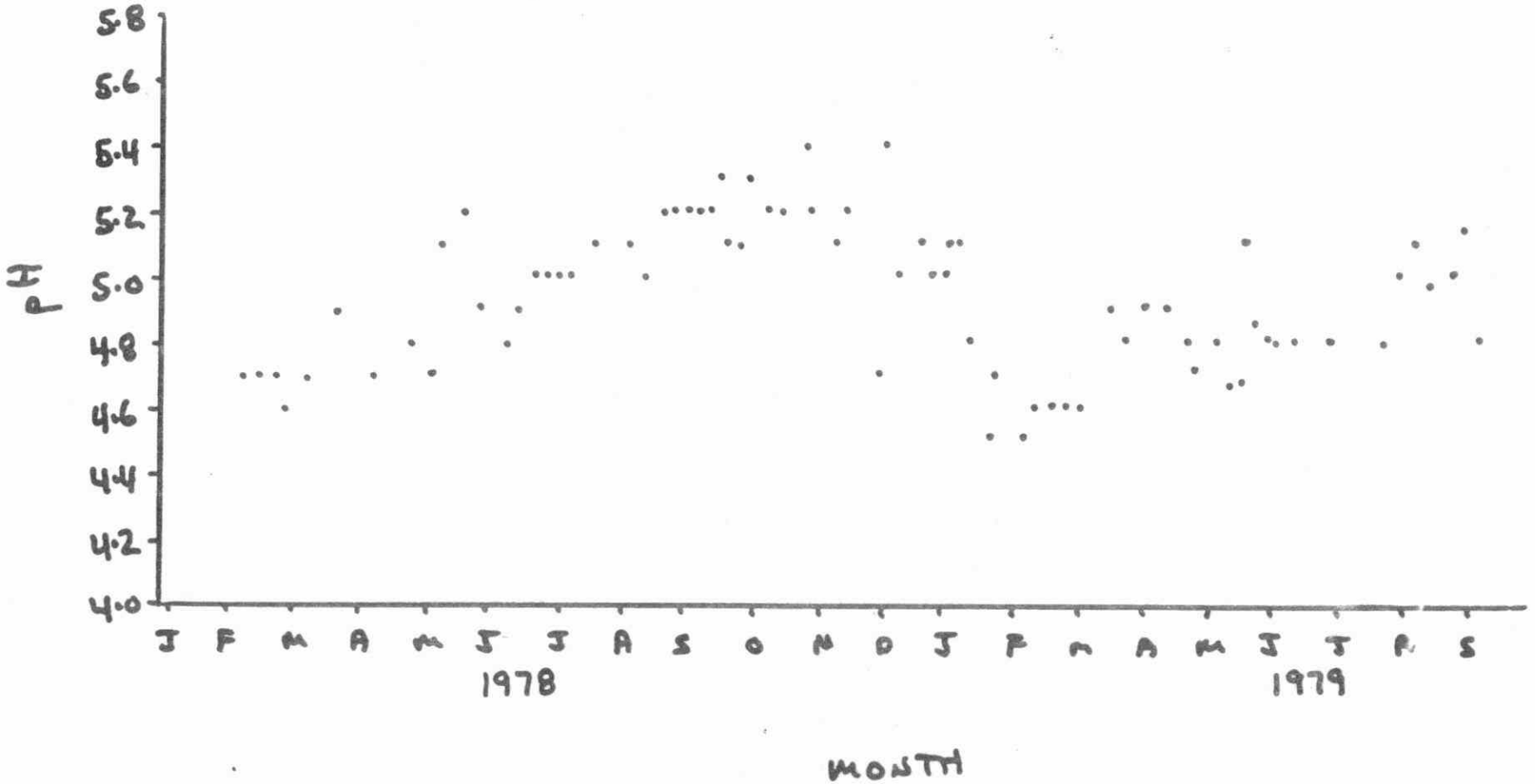


Fig: PEBBIELOGGITCH LAKE pH, Feb 78 - Sept 79 (lab JAMES plotted)

RANGE 4.13 - 4.50
MEAN 4.37

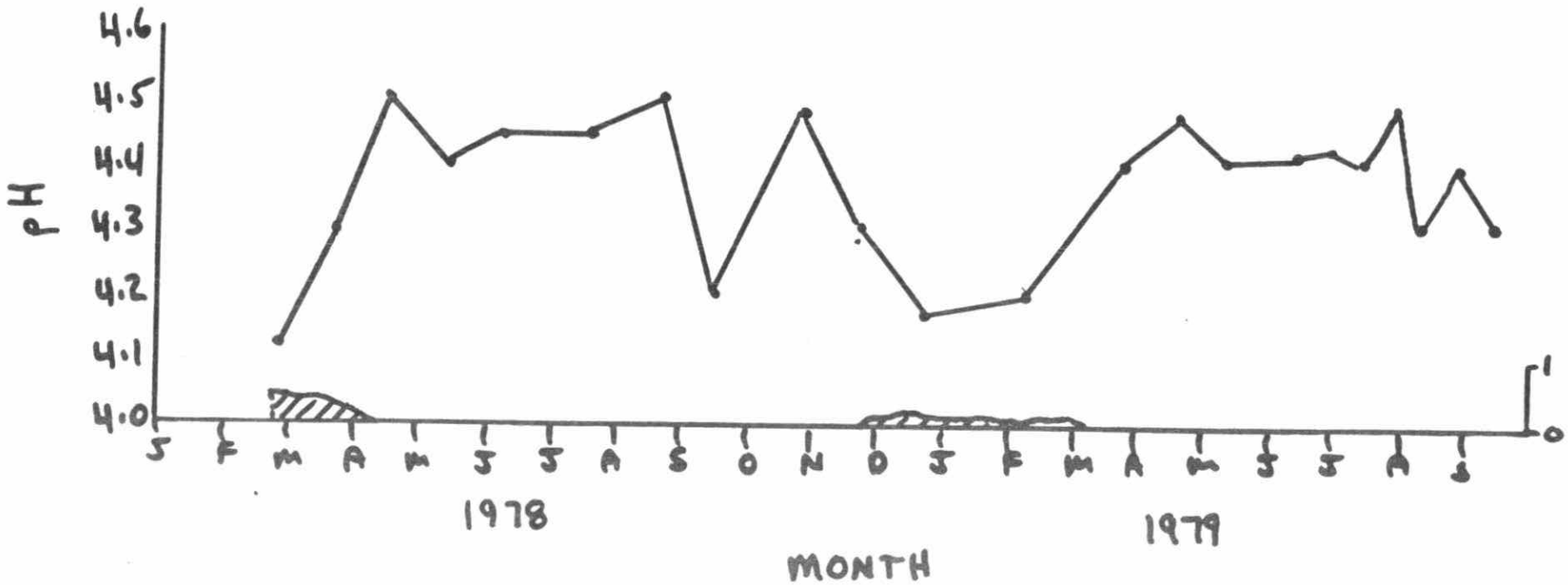
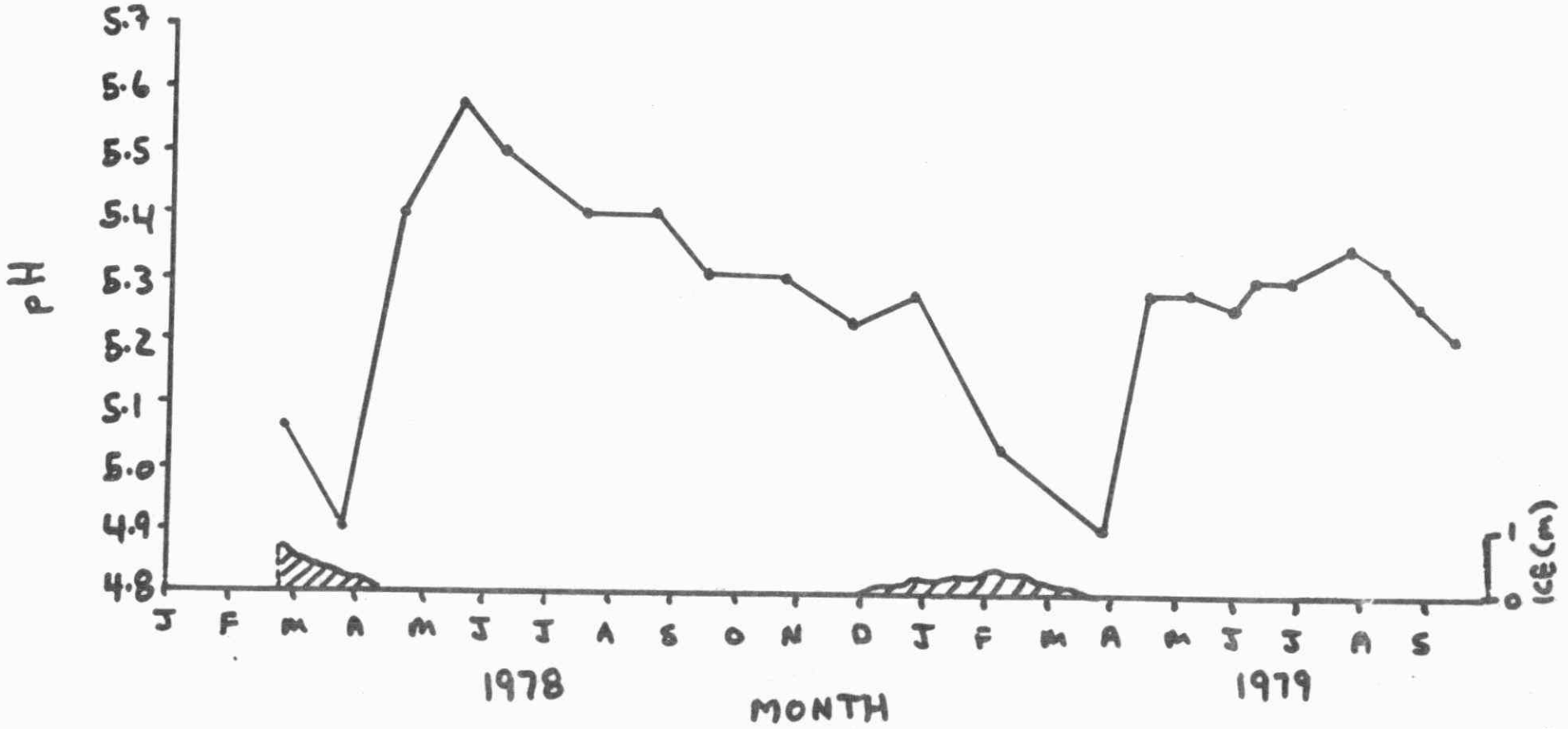


Fig BEAVERSKIN LAKE pH, Feb 78 - Sept 79 (LAB VALUES PLOTTED)

RANGE 4.90 - 5.60
MEAN 5.16



1978 Precipitation

Weighted mean pH values

annual = 4.6

monthly means, range = 4.2 – 5.1

events, range = 3.5 – 6.4

APPENDIX TWENTY

J. R. Kramer

Aluminum in low pH waters -- some preliminary results

Due to reported elevated levels of Al in acidified (circa pH 4-5) waters (1) and their possible toxicity, some initial studies on analysis of Aluminum have been carried out for Canadian waters (LaCloche Mountain area) and from the Hubbard Brook Experimental Forest, Falls Brook, study (1). The method used here is a fluorimetric technique using lumogallion; it is essentially that of Hydes and Liss (2) and details can be found in a recent progress report (3). Samples, both filtered and unfiltered, are obtained in either polytethylene or polypropylene (now only polypropylene) sample bottles. In the comparison with the Falls Brook study, filtered samples through 0.45 μm Millipore samples were analysed, as was done in the reported study. Filters are acid washed for 2 hours with HNO_3 as Al contamination (from the paper separator) is common. All results are from standard addition protocol.

The literature study uses a ferron-orthophenanthroline colorimetric method. This method has a known Fe interference as well as interference with other metals.

Results of analysis show an order of magnitude or greater difference in reported Al results for similar pH's and locations on the Falls Brook stream, with results of this study being lower. They are:

Location	Johnson (1)		This study	
	pH	Al (μm)	pH	Al (μm)
Upper	5.19	5.8	5.99	0.26
	5.54	4.1		
Lower	5.46	1.8	6.13	0.26
	5.59	1.2	5.84	0.15
Hubbard Brook	5.68	1.0	6.04	0.13

Aluminum in low pH waters

The foregoing analyses are for year averages for Johnson and for June 17, 1979, for this preliminary comparison.

Another comparison run was done on October 11, 1979. Here filtered samples were obtained (into acidified solutions) in the field and the pH was measured in the field. Our results are:

	pH	Al (μm)
Upper	4.76	6.3
Middle	4.93	6.9
Lower	5.26	5.8
Hubbard Brook	5.72	6.2 (unfiltered)
Fresh snow composite	4.48	0.59 (unfiltered)

Neither data set are necessarily consistent or inconsistent; however, the wide deviation from the summer results demands that the entire sampling and analysis procedures regarding Aluminum be looked at very carefully.

Results for La Cloche lakes for filtered (field filtered) and unfiltered are for August 26-29, 1979:

Lake	pH	Al (μm)
Quicksilver	4.48	1.33
Nellie (Filt)	4.24	1.15
Nellie	4.24	2.19
Howry	6.33	0.044
Great Mtn.	4.73	.426
Great Mtn. (filt)	4.73	.630
Great Mtn. (10m)	4.77	.538
Killarney	4.63	1.15
Carlyle	4.97	.185
Wright's	6.10	0.0056
Wright's (bot)	6.08	0.011

Although there is an obvious trend with pH, other factors must be considered. We are now considering a reversible neutral surface model after Paces (4). This model involves pH, Si, and Al as variables.

Aluminum in low pH waters

3

Although our data fit the predicted style of equation with very high correlation (r^2 = .996), the values are not at all similar to those of Paces. Our predicted Q function is:

$$\log_{10} Q = 12.1 + 2.61\ pH$$

Research in progress is to develop a complete sampling and analysis procedure for soluble and total Al, then to re-evaluate speciation especially with OH species (very critical in the 4-5 pH range), then to proceed with toxicity tests.

1. Johnson, N. M., Science, 204, p. 497, 1070.

2. Hydes, D. J. and P. S. Liss, Analyst, 101, p. 922-931, 1976.

3. Annual report, Geochemical factors and terrain response to environmental factors, 1979, available upon request from author.

4. Paces, Tomas, Geochimica Cosmochimica Acta, 42, p. 1487, 1978.

GEOCHEMICAL FACTORS AND TERRAIN RESPONSE TO ENVIRONMENTAL CONTAMINANTS

June, 1969

James R. Kramer
Department of Geology
McMaster University
Hamilton, Ontario Canada L8S 4M1
(415-525-9140, ext 4514)

June, 1979.

INTRODUCTION

The following represents results of ongoing research studies relating to the chemistry and geochemistry of softwater regimes. Emphasis is placed upon interaction of soils and rocks with aquatic systems.

Part 1 is a summary of a program of developing a model of chemical flow through a watershed involving surficial, groundwater, and eventually soil and plants. The results are a first survey of a highly unbuffered region in NW Ontario. Soilds in this region consist of glacially derived acidic igneous rocks with kaolinite. This is an ongoing PhD program of W. Booty.

Part 2 gives preliminary results and a method of analysis for Al. This work is being carried out by J. Gleed.

Part 3 gives a method for the accurate interpretation of acid or base titration curves for aquatic systems. The basis of measurement of alkalinity is discussed and various mistakes in applying standard techniques are pointed out. It is hoped that this discussion will lead to more reliable alkalinity measurements for low values in soft water systems.

Part 4 is a summary of stream crossing data collected for Ontario and Quebec this year and in the past two years. Areas susceptible to acid precipitation in all of Ontario and portions of quebec are shown.

TABLE OF CONTENTS

		Page
PART 1	AQUATIC AND SOIL CHEMISTRY, NORTHWESTERN ONTARIO Acid susceptibility and flow model	1
PART 2	ALUMINUM IN WATER: PRELIMINARY RESULTS	52
PART 3	ALKALINITY MEASUREMENTS IN SOFT WATERS	60
PART 4	SUSCEPTIBLE AREAS IN ONTARIO AND QUEBEC	76

PART 1

AQUATIC AND SOIL CHEMISTRY, NORTHWESTERN ONTARIO

Acid susceptibility and flow model

TABLE OF CONTENTS

		Page
I.	INTRODUCTION	1
II.	STUDY	4
	(a) Lake Survey	4
	(b) Soil Survey	5
	(c) Precipitation Survey	7
III.	RESULTS	8
	(a) Lakewater	8
	(b) Soil and Overburden	20
	(c) Precipitation	24
IV.	DISCUSSION	27
V.	FUTURE WORK	38

LIST OF FIGURES

Figure		Page
1	1978 Study Area Coverage	3
2	Water Sample Locations	14
3	Watershed Map	18
4	Soil Sample Locations	22
5	Calcite Saturation Index (CSI) Contour Map	30
6	Susceptible Portion (CSI>3) of the 1978 Study Area	31
7	Relationship of Specific Conductivity and Alkalinity of Water Samples	32
8	Comparison of MNR and this Study Specific Conductivity Measurements	34
9	Comparison of MNR and this Study Alkalinity Measurements	35
10	H^+-Exchange Capacity *vs.* Solution pH Relationship for A.P.I. Reference Clays and Clay Size Fraction of Soils from this Study	37
11	Schematic of Flow System of Watershed Model	41

LIST OF TABLES

Table		Page
1	Chemistry of Lakewater and Streamwater Samples	9
2	Water Sample Locations	15
3	Soil Sample Locations	21
4	Sediment Size Analysis	23
5	H^+-Exchange Capacity of Soil Samples and Standard Clays	25
6	Calcite Saturation Index of Water Samples	29
7	Flow Model Notation	40

I. INTRODUCTION

The waterways in the Quetico-Atikokan region were noticed as being poorly buffered in a Provincial stream-crossing survey (Kramer, 1977). Hence this remote region would be susceptible to acid rainfall. The area includes Quetico Provincial Park and is near the Boundary Waters Canoe Area (BWCA), Minnesota. The area represents a susceptible terrain which is affected by long distance transport of atmospheric pollutants. There are no major local or regional sources. The closure of Steep Rock Mines and concern over effects from development of the Atikokan fossil fuel electrical generating plant warrant intensive study relative to terrain response to environmental contaminants. The area is also considered because of the controlled access to Quetico Provincial Park which allows assessment of predominantly natural changes. This report contains the results of an initial survey of lakes and soil of the Quetico-Atikokan region, which is supplemented by Ministry of Natural Resources data. Assistance by personnel of the Ministry of Natural Resources in Toronto and Atikokan is acknowledged in providing information for the area.

The study consisted of a field sampling program coupled with a base camp laboratory. The survey teams consisted of 2 canoe parties, which carried out most of their work within Quetico Provincial Park, and 1 vehicle team, which studied the watersheds outside of the park boundary. The teams studied the lakes in soil in exposed cuts and by the use of hand augers. The 1978 study area coverage is shown (hachured) in Figure 1.

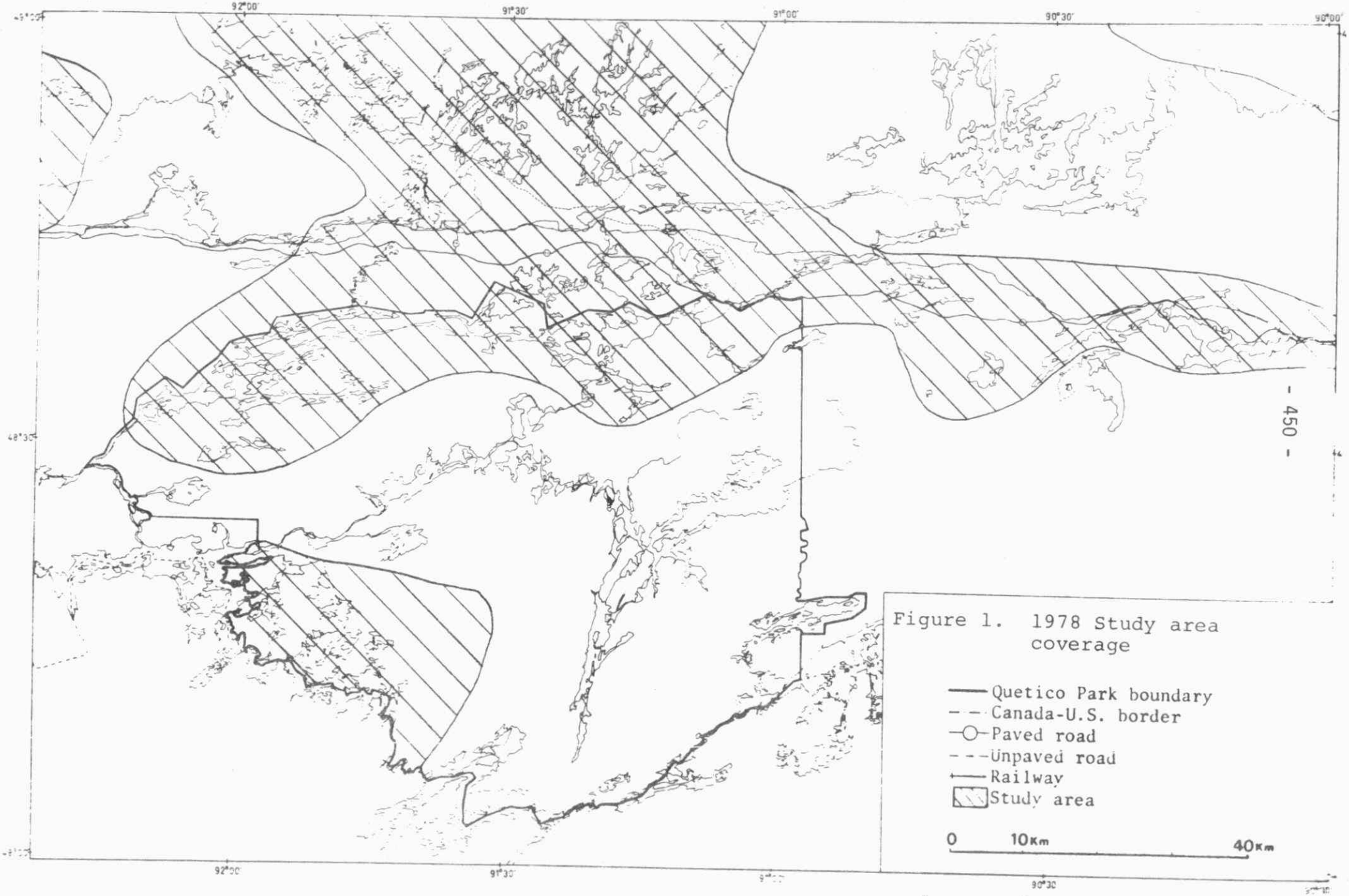


Figure 1. 1978 Study area coverage

II. STUDY

(a) Lake Survey

Variables measured in the field were pH, specific conductivity, temperature, and secchi depth. Water samples were collected for determination of alkalinity, chlorophyll, and phytoplankton at the field laboratory. Typically, a 6 m integrated depth sample and a sample at 10 m depth or 1 m above the bottom were collected by the canoe parties. Samples (acidified) were also collected for metals at a number of the sample locations.

In the chlorophyll procedure, a known volume of water was filtered through a GFC filter. The filter was then covered with a $MgCO_3$ solution and immediately stored in a blacked-out dessicator for subsequent laboratory analysis.

In the phytoplankton procedure, a known volume of water was filtered through a 0.45 micron membrane filter. The filter was immediately treated with a formaldehyde solution and stored in a petri dish.

The pH of the lake surface waters was measured directly from the canoe using a portable, digital pH meter.

Specific conductance and temperature of the water samples were also measured in the field.

The alkalinities of the integrated and depth water samples (unfiltered) were determined by a Gran analysis of laboratory acid titration data. A laboratory determination of hardness, pH, and conductivity was also performed on the integrated and depth water samples.

(b) Soil Survey

Variables measured in the field were soil colour, depth and thickness of units. A size analysis and the hydrogen-exchange capacity of the soils has been carried out at the geochemical laboratories at McMaster University. A determination of the clay mineralogy of the soils has yet to be completed.

The natural soil samples were air-dried and sieved. The clay-size fraction (<0.004 mm) was used in the quantitative study of the H-exchange capacity (buffering) of the soil samples. A final soil solution ratio of 1:50 was used for all of the titrations. The solution is made to constant ionic strength by the addition of a neutral salt. The effect of cation competition at the exchange sites between

H^+ and the salt cation is evaluated by comparing the results obtained for 0.01 M and 0.001 M NaCl and 0.01 M and 0.001 M $CaCl_2$ solutions.

The soil solutions were mixed with a magnetic stirrer for 2 hrs before being titrated. The titrant concentrations are either 0.1 or 0.01 eq/ℓ depending on the exchange capacity of the sample. The acid is supplied to the sample at a constant rate (0.039 ml/min) by a paristaltic pump. The pH of the soil solution is measured with a digital pH meter which is coupled to an automatic electrode switching unit. This allows several samples to be titrated simultaneously. A printer is used to record the pH at 1 minute intervals. The sample is titrated to pH 3.0-3.5. Blank samples of constant ionic strength are titrated to allow corrections to be made to the measured pH values of the soil solutions.

The hydrogen-exchange capacity of the soil sample for the given pH range is given by

$$H^+.E.C. = C_A V_A - (V_S + V_A)10^{-pH_f} \quad \text{(meq/gm)}$$

C_A = concentration of acid added (meq/ml)

V_A = volume of acid (ml)

V_S = volume of sample (ml)

The H^+ exchange capacity per unit weight of sample (meq/100 g) is then determined. The amount of H^+ ions adsorbed versus the solution pH is plotted to determine the nature of the adsorption function.

(c) Precipitation Survey

Samples of precipitation were collected at the field laboratory for chemical analysis.

III. RESULTS

Table 1 contains the results of the analytical studies of the water samples. The locations of the water samples are shown on Figure 2. The numbers on the map correspond to the sequence numbers in column 1 of Table 1. Table 2 contains a list of the study lakes and their corresponding latitude, longitude, and watershed. Figure 3 shows the boundaries of the watersheds and their MNR code number in their water surveys.

(a) Lakewater

Conductivity ranged from 11 to 425 µmho/cm (25°C). Most lakes (87%) have specific conductivities less than 60 µmho/cm. None of the lakes within Quetico Provincial Park had a specific conductivity greater than 50 µmho/cm. The average specific conductivity of the lakewater studied within Quetico Provincial Park is 22.9 µmho/cm. Alkalinity in the study lakes ranges from 3.18×10^{-5} eq/ℓ to 1.47×10^{-3} eq/ℓ. The average alkalinity within the park is 1.40×10^{-4} eq/ℓ. The field measured surface pH varied

Table 1. Chemistry of Lakewater and Streamwater Samples

Seq. No.	Sample No.	Location	Date	Depth (m)	Field pH	Lab pH	Secchi Depth (m)	Spec Cond (μmho/cm) 25°C	Temp °C	Alkalinity as HCO_3^- (eq/l)	pAlk	Chloro-a (mg/m^3)	Pheo (mg/m^3)
1	78-B-1	Eva L.	78-07-11	Int 1.5	6.75	6.82	4.5	33.0	19	1.67E-04	3.777	0.29	1.43
2	78-B-2	W. Nym L.	78-07-12	Int 1.5	6.80	6.82	4.0		19	1.04E-04	3.983	0.00	2.64
	78-B-2	"	"	10.0		6.85				9.86E-05	4.006		
3	78-B-3	Batchewaung L.	"	12.0	6.55	6.59	3.5	21.5	18.5	9.88E-05	4.006		
	"	"	"	Int 1.5						9.82E-05	4.008	0.15	0.50
4	78-B-4	Lerome L.	78-07-13	Int 1.5	7.35	6.94	3.3	33.5	19	2.51E-04	3.601	0.00	4.40
	"	"	"	9.0		6.45				2.61E-04	3.583		
5	78-B-5	Unamed L.	"	Int 1.5	7.05	6.14	1.6	23.0	19	3.27E-04	3.486	0.60	4.50
6	78-B-6	Bewag L.	"	Int 1.5	6.85	6.99	3.5	26.2	19.5	2.10E-04	3.679	0.30	3.60
	"	"	"	10.0		6.66				2.28E-04	3.643		
7	78-B-7	Lark L.	"	Int 1.5	6.30	6.00	2.0	14.2	19.5	6.46E-05	4.190	0.00	5.60
	"	"	"	10.0		6.15				5.76E-05	4.239		
8	78-B-8	Cole L.	78-07-14	Int 1.5	6.70	6.33	2.0	17.0	19	8.13E-05	4.090	0.30	4.80
	"	"	"	10.0		6.14				8.48E-05	4.072		
9	78-B-9	Soho L.	"	Int 1.5	6.25	6.79	4.0	19.6	19	9.88E-05	4.005	0.30	1.00
	"	"	"	10.0		6.72				9.98E-05	4.001		
10	78-B-10	Smudge L.	"	Int 1.5	6.25	6.47	2.0	19.0	21	8.14E-05	4.889	0.00	11.00
	"	"	"	10.0		6.43				7.62E-05	4.118		
11	78-B-11	Cirrus L.	"	Int 1.5	6.85	6.35	4.8	18.3	20.5	9.35E-05	4.029	0.00	12.00
	"	"	"	10.0		6.76				9.46E-05	4.024		
12	78-B-12	Gardner Bay	78-07-20	Int 6.0		6.75	4.0	23.6	21	1.34E-04	3.871	2.40	0.50
	"	"	"	8.0		6.07				1.51E-04	3.820		
13	78-B-13	Gardner-Elk	"	Int 6.0	5.90	6.46		21.2	23	1.29E-04	3.891	1.60	1.40
14	78-B-14	Elk L.	"	"	7.40	6.87	6.0	21	23	1.26E-04	3.901	0.90	2.20
	"	"	"	8.0		6.85				1.29E-04	3.889		
15	78-B-15	Hurn L.	78-07-21	Int 6.0		6.87	4.8	21.2	23	1.20E-04	3.920	1.30	0.00
	"	"	"	8.0		6.33				1.36E-04	3.867		

Table 1/continued

Seq. No.	Sample No.	Location	Date	Depth (m)	Field pH	Lab pH	Secchi Depth (m)	Spec Cond (μmho/cm) 25°C	Temp °C	Alkalinity as HCO_3^- (eq/l)	pAlk	Chloro-a (mg/m^3)	Pheo (mg/m^3)
16	78-B-16	Elk-Cone	"	Int 2.0	6.75	6.60	3.0	20.2	24	1.17E-04	3.930	2.40	2.80
17	78-B-17	Cone L.	"	Int 6.0	6.40	6.88	7.5	19.5	22	1.09E-04	3.961	0.50	1.00
	"	"	"	10.0		6.65				1.18E-04	3.928		
18	78-B-18	Cone-Argo	"	Int 6.0	7.10	6.83	5.0	22.8	22	1.03E-04	3.989	0.00	2.00
	"	"	"	6.0		6.08				1.26E-04	3.901		
19	78-B-19	Brewer L.	78-07-22	Int 6.0		7.02	2.5	47.3	19.5	3.08E-04	3.511	1.90	1.80
	"	"	"	6.0		7.07				3.07E-04	3.513		
20	78-B-21	Little McCaulay L.	78-07-25	1.0	6.90	6.94		48.6	23.5	2.68E-04	3.573		
21	78-B-22	Manion L.	78-07-25	1.0	7.15	7.09	--	29.4	25	1.64E-04	3.786	--	--
22	78-B-23	Dashwa L.	78-07-26	Int 6.0		6.82	5.2	24.0	22	9.79E-05	4.009	0.00	0.70
	"	"	"	10.0									
23	78-B-24	Turtle L.	"	Int 6.0		6.69	3.2	24.4	22	9.71E-05	4.013		
24	78-B-25	Niobe L.	"	1.0		6.79		43.0	22	1.58E-04	3.801		
25	78-M-2	Gillnet L.	78-07-12	Int 6.0	6.90	6.00	2.3	21.0	19	8.65E-05	4.063	3.79	2.94
	"	"	"	10.0		6.30				7.67E-05	4.115		
26	78-M-3	Black Bay	"	Int 6.0	5.54	5.51	1.5	22.0	19	5.06E-05	4.296	0.11	3.67
	"	"	"	11.0		5.90				1.62E-04	3.791		
27	78-M-4	Bearpelt L.	78-07-15	Int 6.5		6.64	1.5	31.0	20	1.52E-04	3.817	0.20	3.00
28	78-M-5	Omeme L.	"	Int 6.5		6.46	2.0	22.0	19	1.11E-04	3.956	5.90	0.00
29	78-M-6	Bee L.	"	Int 6.0		6.48	2.5	18.0	20	1.02E-04	3.993	0.00	3.50
	"	"	"	8.0		5.89				1.08E-04	3.967		
30	78-M-7	Badwater L.	"	Int 6.0		6.56	2.5	20.0	19	1.02E-04	3.992		
31	78-M-8	Unamed L.	78-07-16	Int 6.0		6.66	1.5	32.0	22	2.00E-04	3.710	8.20	0.00
	"	"	"	6.0		6.59				1.95E-04	3.700		
32	78-M-9	West Bay	"	Int 6.0		6.74	2.5	25.0	21	1.42E-04	3.849	0.00	8.10
	"	"	"	7.0		6.24				1.61E-04	3.794		

Table 1/continued

Seq. No.	Sample No.	Location	Date	Depth (m)	Field pH	Lab pH	Secchi Depth (m)	Spec Cond (μmho/cm) 25°C	Temp °C	Alkalinity as HCO_3^- (eq/1)	pAlk	Chloro-a (mg/m^3)	Pheo (mg/m^3)
33	78-M-10	Quetico L.	"	Int 6.0		6.85	4.0	23.0	19	1.24E-04	3.906	2.30	1.40
34	78-M-11	Beaverhouse L.	"	Int 6.0		6.79	5.0	23.0	22	1.25E-04	3.902	11.40	0.00
35	78-M-12	McAree L.	78-07-19	Int 6.0		7.01	4.5	26.0	22	2.09E-04	3.680	2.10	1.10
	"	"	"	17.0		6.41				2.18E-04	3.661		
36	78-M-13	Minn L.	"	Int 6.0		6.56	2.5	16.0	22	7.78E-05	4.109	1.00	2.20
	"	"	"	6.5		6.18				8.56E-05	4.062		
37	78-M-14	Wicksteed L.	"	Int 6.0		6.58	4.5	18.5	21	1.02E-04	3.992	2.20	0.00
38	78-M-15	Darky L.	"	Int 6.0		6.61	4.5	18.0	22	8.23E-05	4.085	0.30	1.60
39	78-M-16	Ballard L	"	Int 6.0		6.62	4.5	18.5	23	8.93E-05	4.049	0.00	2.70
40	78-M-17	Darky R.	"	Int 6.0		6.52	4.0	17.9	23	7.39E-05	4.131	0.30	2.60
41	78-M-18	Argo L.	78-07-20	Int 6.0		6.94	6.5	19.0	"	1.23E-04	3.909	0.00	0.50
42	78-M-19	Roland L.	"	Int 6.0		6.89	4.5	17.0	20	1.06E-04	3.975	0.00	4.90
	"	"	"	24.0		6.16				1.09E-04	3.964		
43	78-M-20	M. Roland L.	"	Int 6.0		6.76	4.5	17.0	22	1.04E-04	3.984	0.30	2.30
	78-M-21	"	"	Int 3.0		6.62				1.12E-04	3.951		
44	78-M-22	McAree L.	"	Int 6.0		7.07	2.0	40.0	20	2.76E-04	3.560	0.00	5.80
	"	"	"	11.0		6.90				2.99E-04	3.524		
45	78-M-23	Lac LaCroix	"	Int 6.0		7.00	2.7	37.0	20	2.98E-04	3.526	1.20	1.50
	"	"	"	16.5		7.01				2.92E-04	3.534		
46	78-M-24	Unamed L.	78-07-25	Int 6.0		6.93	3.3	20	21	1.16E-04	3.937	0.00	5.50
	"	"	"	8.0		6.14				1.88E-04	3.725		
47	78-M-25	Buckingham L.	"	Int 6.0		6.75	3.3	20	21	8.28E-05	4.082	0.00	3.80
	"	"	"	10.0		6.19				9.21E-05	4.036		
48	78-M-26	Art L.	"	Int 3.0		6.77	3.5	23	21	8.74E-05	4.059	0.50	2.00
	"	"	"	5.0		6.57				8.49E-05	4.071		

Table 1/continued

Seq. No.	Sample No.	Location	Date	Depth (m)	Field pH	Lab pH	Secchi Depth (m)	Spec Cond (μmho/cm) 25°C	Temp °C	Alkalinity as HCO_3^- (eq/l)	pAlk	Chloro-a (mg/m^3)	Pheo (mg/m^3)
49	78-M-27	Fosberg L.	78-07-26	Int 3.0		6.51	3.5	16.0	21	8.95E-05	4.048	0.00	3.90
	"	"	"	6.0									
50	78-M-28	Williamson L.	"	Int 3.0		6.35	1.8	16.0	21	7.37E-05	4.132	2.10	1.30
51	78-K-1	Windigoostigwan L.	78-07-12	1.0	6.60	6.60	--	22.0	20	1.09E-04	3.963	--	--
52	78-K-2	Unamed	"	1.0		5.80		22.5	20	3.16E-05	4.498		
53	78-K-3	Arbour L.	"	1.0		6.69		31.0	20	6.39E-05	4.195		
54	78-K-4	Crayfish Cr.	"	1.0		6.29		37.5	20	6.97E-05	4.157		
55	78-K-5	Laughren L.-Cr.	"	1.0		5.63		33.5	17	9.61E-05	4.017		
56	78-K-6	Unamed L.	"	1.0		6.59		19.0	20.5	6.67E-05	4.176		
57	78-K-7	Huronian L.	"	1.0		6.84		22.0	20	7.84E-05	4.106		
58	78-K-8	Swamp R.	78-07-14	1.0		6.75		49.0	20.5	3.64E-04	3.439		
59	78-K-10	Middle Shebandowan L.	"	"		7.12		111.0	20	6.79E-04	3.168		
60	78-K-12	Upper Shebandowan L.	"	"		7.52		108.0	21	6.56E-04	3.183		
61	78-K-13	Unamed L.	"	"		7.36		162.0	20	6.52E-04	3.185		
62	78-K-14	Unamed R.	"	"		6.78		34.5	19.5	2.16E-04	3.665		
63	78-K-15	Unamed L.	"	"		7.59		90.0	20.5	6.93E-04	3.159		
64	78-K-16	Burchell L.	"	"		7.52		76	20	4.47E-04	3.349		
65	78-K-18	Rainbow L.	"	"		7.35		84.0	21	7.16E-04	3.145		
66	78-K-20	Pickerel R.	78-07-16	"	7.10	6.92		29.5	20	1.75E-04	3.756		
67	78-K-21	French R.	"	"	7.05	6.84		26.8	20	1.30E-04	3.886		
68	78-K-22	Far L.	"	"	7.40	7.14		41.0	23	2.83E-04	3.549		
69	78-K-23	Kabaigon L.	"	"	7.85	7.61		73.0	25	6.20E-04	3.208		
70	78-K-24	Amp L.	"	"	7.60	7.40		63.0	23.5	5.21E-04	3.283		
71	78-K-25	Camp Quetico	78-07-11	Rain	3.85	3.85		8.0					
72	78-K-26	Melema L.	78-07-19	1.0		6.77		31.0	22	1.97E-04	3.707		
73	78-K-27	Seine R.	"	"		6.83		45.0	22	3.32E-04	3.479		
74	78-K-28	Bickford Drain	"	"		6.37		24.0	22	1.37E-04	3.864		

Table 2/continued

Seq. No.	Sample No.	Location	Date	Depth (m)	Field pH	Lab pH	Secchi Depth (m)	Spec Cond (μmho/cm 25°C)	Temp °C	Alkalinity as HCO_3^- (eq/l)	pAlk	Chloro-a (mg/m^3)	Pheo (mg/m^3)
75	78-K-29	Un. Headwater L.	"	"		6.37		25.0	23	1.29E-04	3.889		
76	78-K-30	Caskill L.	"	"		6.49		22.5	23	1.30E-04	3.887		
77	78-K-32	Un. Headwater L.	"	"		6.61		25.0	22	1.76E-04	3.755		
78	78-K-33	Premier L.	"	"		6.86		41.0	21	2.79E-04	3.555		
79	78-K-34	St. Patrick Cr.	"	"		6.60		35.0	22	2.20E-04	3.658		
80	78-K-35	Keckusch L.	"	"		6.60		28.0	21	1.57E-04	3.806		
81	78-K-36	Nowquabic L.	"	"		7.72		85.0	20	6.92E-04	3.160		
82	78-K-37	Wabash L.	"	"		7.13		55.0	20	4.08E-04	3.390		
83	78-K-38	Atikokan R.	"	"		6.98		52.0	20	4.06E-04	3.392		
84	78-K-39	Kawene L.	"	"		6.55		29.0	20	1.63E-04	3.788		
85	78-K-40	Icy L.	78-07-21	"		7.68		136.0	19	1.07E-03	2.971		
86	78-K-41	Fotheringham L.	"	"		6.84		42.0	20	2.93E-04	3.533		
87	78-K-43	Snow L.	"	"		7.34		64.0	20	4.88E-04	3.311		
88	78-K-44	Moose L.	"	"		7.64		131.0	20	1.10E-03	2.958		
89	78-K-45	Marmion L.	"	"		7.68		133.0	20	6.71E-04	3.173		
90	78-K-46	N. Twin L.	"	"		8.63		425	20	1.47E-03	2.832		
91	78-K-47	Findlayson L.	"	"		7.22		43.0	20	2.75E-04	3.561		
92	78-K-48	Hardtack R.	"	"		5.80		16.0	20	7.59E-05	4.120		
93	78-K-50	Dashwa L.	"	"		6.87		19.0	20	9.97E-05	4.001		
94	78-K-51	Eye L.	"	"		6.72		27.0	20	1.04E-04	3.984		
95	78-K-52	Williamson L.	"	"		6.34		19.0	20.5	6.89E-05	4.162		
96	78-K-53	Knight L.	"	"		6.13		11.0	20	2.86E-05	4.543		
97	78-K-54	Turtle L.	"	"		6.64		21	22	9.71E-05	4.013		
98	78-K-55	Clearwater L.	"	"		6.84		22.0	22	1.53E-04	3.816		
99	78-K-57	Slim L.	"	"		5.75		16.0	23	3.59E-05	4.445		
100	78-K-58	Halfmoon L.	"	"		6.90		22.0	22	1.42E-04	3.848		
101	78-K-59	Turtle L.-R.	"	"		6.94		19.0	21	1.06E-04	3.974		
102	78-PB-20	Rawn L.	78-07-25	Int 6.0		6.62	3.0	23.0	20.5	9.54E-05	4.021	1.30	2.00
	"	"	"	10.0		6.14				9.67E-05	4.015		
103	78-PB-21	W. Pickerel L.	"	Int 6.0		6.93	4.0	23.0	23.5	1.15E-04	3.939	1.30	2.00
	"	"	"	10.0		6.59				1.28E-04	3.892		
104	78-PB-22	E. Pickerel L.	"	Int 6.0		6.98	3.5	26.0	22	1.30E-04	3.885	0.20	2.40
	"	"	"	10.0		6.95				1.26E-04	3.894		

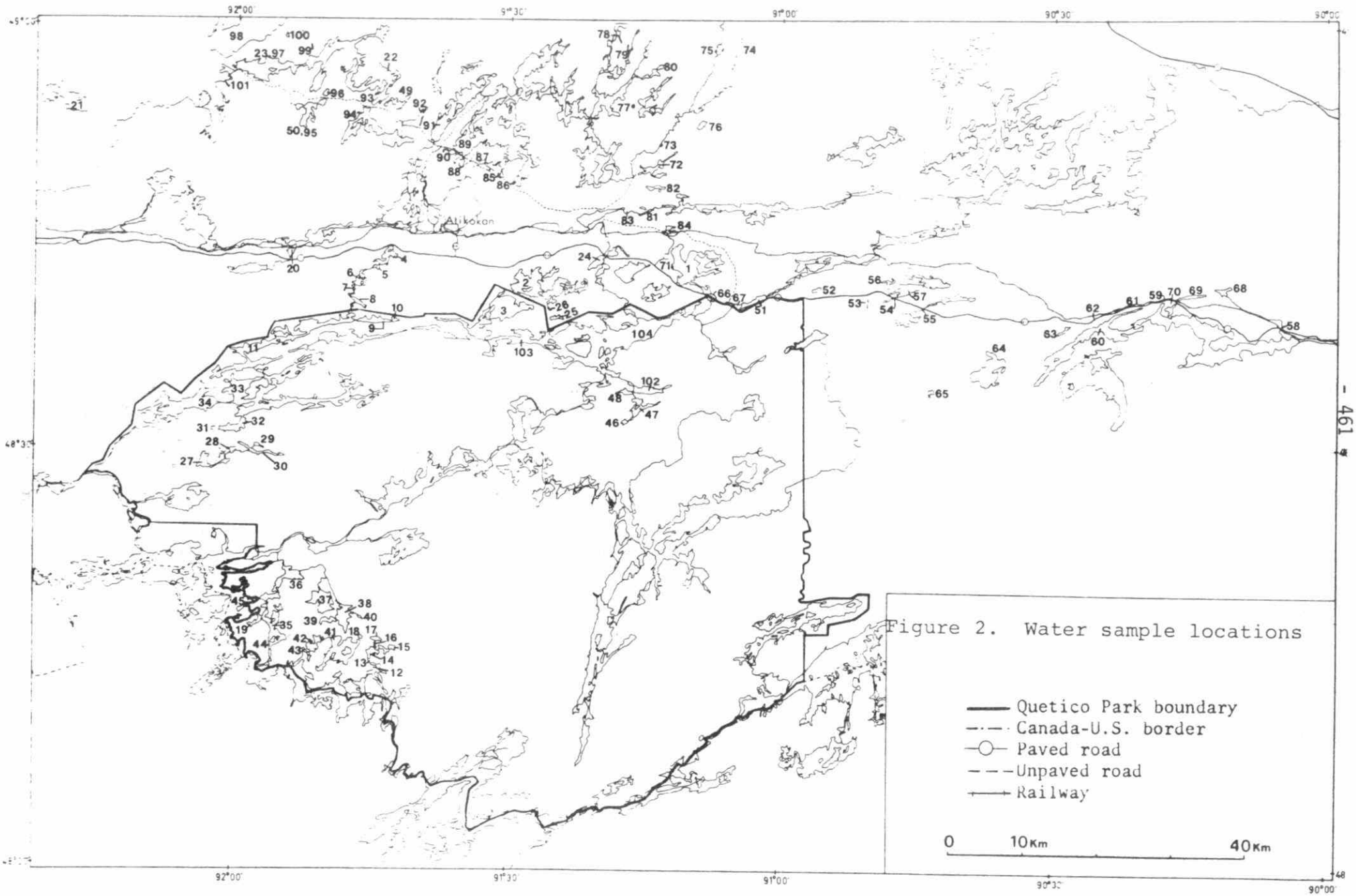


Figure 2. Water sample locations

Table 2. Water Sample Locations

Map No.	Location	Lat.	Long.	Watershed
1	Eva L.	48 43	91 10	5 PA-3
2	Nym L.	48 42	91 26	5 PA-3
3	Batchewaung L.	48 40	91 30	5 PA-3
4	Lerome L.	48 44	91 44	5 PB-18
5	Unnamed L.	48 44	91 44	5 PB-18
6	Bewag L.	48 41	91 47	5 PB-18
7	Lark L.	48 40	91 48	5 PA-2
8	Cole L.	48 40	91 47	5 PA-2
9	Soho L.	48 39	91 45	5 PA-2
10	Smudge L.	48 39	91 41	5 PA-2
11	Cirrus L.	48 37	91 55	5 PA-2
12	Gardner Bay	48 13	91 45	5 PA-4
13	Gardner-Elk	48 15	91 45	5 PA-4
14	Elk L.	48 16	91 45	5 PA-4
15	Hurn L.	48 16	91 43	5 PA-4
16	Elk-Cone	48 16	91 44	5 PA-4
17	Cone L.	48 17	91 45	5 PA-4
18	Cone-Argo	48 17	91 46	5 PA-4
19	Brewer L.	48 17	91 58	5 PA-4
20	Little McCaulay L.	48 44	91 54	5 PB-18
21	Manion L.	48 52	92 21	5 PB-16
22	Dashwa L.	48 56	91 45	5 PB-17
23	Turtle L.	48 55	92 00	5 PB-17
24	Niobe L.	48 43	91 20	5 PA-3
25	Gillnet L.	48 37	91 27	5 PA-3
26	Black Bay	48 37	91 27	5 PA-3
27	Bearpelt L.	48 29	92 02	5 PA-2
28	Omeme L.	48 30	92 00	5 PA-2
29	Bee L.	48 30	91 57	5 PA-2
30	Badwater L.	48 29	91 57	5 PA-2
31	Unnamed L.	48 32	92 01	5 PA-2
32	West Bay	48 33	92 00	5 PA-2
33	Quetico L.	48 34	91 55	5 PA-2
34	Beaverhouse L.	48 33	92 06	5 PA-2
35	McAree L.	48 16	91 55	5 PA-4
36	Minn L.	48 21	41 58	5 PA-4
37	Wicksteed L.	48 19	91 50	5 PA-4
38	Darky L.	48 18	91 47	5 PA-4
39	Ballard L.	48 18	91 49	5 PA-4
40	Darky R.	48 21	91 51	5 PA-4
41	Argo L.	48 15	91 48	5 PA-4
42	Roland L.	48 15	91 51	5 PA-4

Table 2/continued

Map No.	Location	Lat.	Long.	Watershed
43	M. Roland L.	48 15	91 51	5 PA-4
44	McAree L.	48 18	91 56	5 PA-4
45	Lac La Croix L.	48 17	91 59	5 PA-4
46	Unnamed L.	48 32	91 18	5 PA-3
47	Buckingham L.	48 33	91 15	5 PA-3
48	Art L.	48 34	91 59	5 PA-4
49	Fosberg L.	48 54	91 44	5 PB-21
50	Williamson L.	48 54	91 52	5 PB-21
51	Windigoostigwan L.	48 43	90 56	5 PA-3
52	Unnamed L.	48 41	90 56	5 PA-3
53	Arbour L.	48 40	90 51	5 PA-5
54	Crayfish Cr.	48 38	90 46	2 AB-12
55	Laughren L.-Cr.	48 39	90 45	5 PA-5
56	Unnamed L.	48 42	90 50	2 AB-12
57	Huronian L.	48 41	90 47	2 AB-12
58	Swamp R.	48 37	90 06	2 AB-5
59	Middle Shebandowan L.	48 40	90 18	2 AB-11
60	Upper Shebandowan L.	48 38	90 27	2 AB-11
61	Unnamed L.	48 39	90 25	2 AB-11
62	Unnamed R.	48 39	90 26	2 AB-12
63	Unnamed L.	48 37	90 30	2 AB-11
64	Burchell L.	48 36	90 37	5 PA-5
65	Rainbow L.	48 33	90 45	5 PA-5
66	Pickerel R.	48 39	91 07	5 PA-3
67	French R.	48 39	91 06	5 PA-3
68	Far L.	48 41	90 13	2 AB-5
69	Kabaigon L.	48 40	90 15	2 AB-12
70	Amp L.	48 39	90 18	2 AB-11
71	Camp Quetico	48 42	91 12	5 PA-3
72	Melema L.	48 50	91 15	5 PB-2
73	Seine R.	48 51	91 16	5 PB-18
74	Bickford L. Cr.	48 56	91 07	5 PB-18
75	Un. Headwater L.	48 57	91 09	5 PB-18
76	Caskill L.	48 53	91 08	5 PB-18
77	Un. Headwater L.	48 53	91 09	5 PB-18
78	Premier L.	49 00	91 18	5 PB-18
79	St. Patrick Cr.	48 58	91 16	5 PB-18
80	Keckusch L.	48 57	91 15	5 PB-18
81	Nowquabic L.	48 46	91 15	5 PB-22
82	Wabash L.	48 48	91 15	5 PB-23
83	Atikokan R.	48 46	91 16	5 PB-22

Table 2/continued

Map No.	Location	Lat.	Long.	Watershed
84	Kawene L.	48 45	91 13	5 PA-3
85	Icy L.	48 50	91 32	5 PB-18
86	Fotheringham L.	48 48	91 32	5 PB-18
87	Snow L.	48 51	91 34	5 PB-18
88	Moose L.	48 50	91 35	5 PB-18
89	Marmion L.	48 52	91 34	5 PB-18
90	N. Twin L.	48 52	91 36	5 PB-18
91	Findlayson L.	48 55	91 34	5 PB-18
92	Hardtack R.	48 56	91 38	5 PB-21
93	Dashwa L.	48 56	91 45	5 PB-17
94	Eye L.	48 52	91 44	5 PB-21
95	Williamson L.	48 53	91 54	5 PB-21
96	Knight L.	48 55	91 53	5 PB-17
97	Turtle L.	48 57	91 57	5 PB-17
98	Clearwater L.	49 00	91 57	5 PB-10
99	Slim L.	48 58	91 53	5 PB-17
100	Halfmoor L.	49 59	91 55	5 PB-10
101	Turtle R.	48 57	92 01	5 PB-17
102	Rawn L.	48 34	91 15	5 PA-3
103	W. Pickerel L.	48 37	91 26	5 PA-3
104	E. Pickerel L.	48 37	91 16	5 PA-3

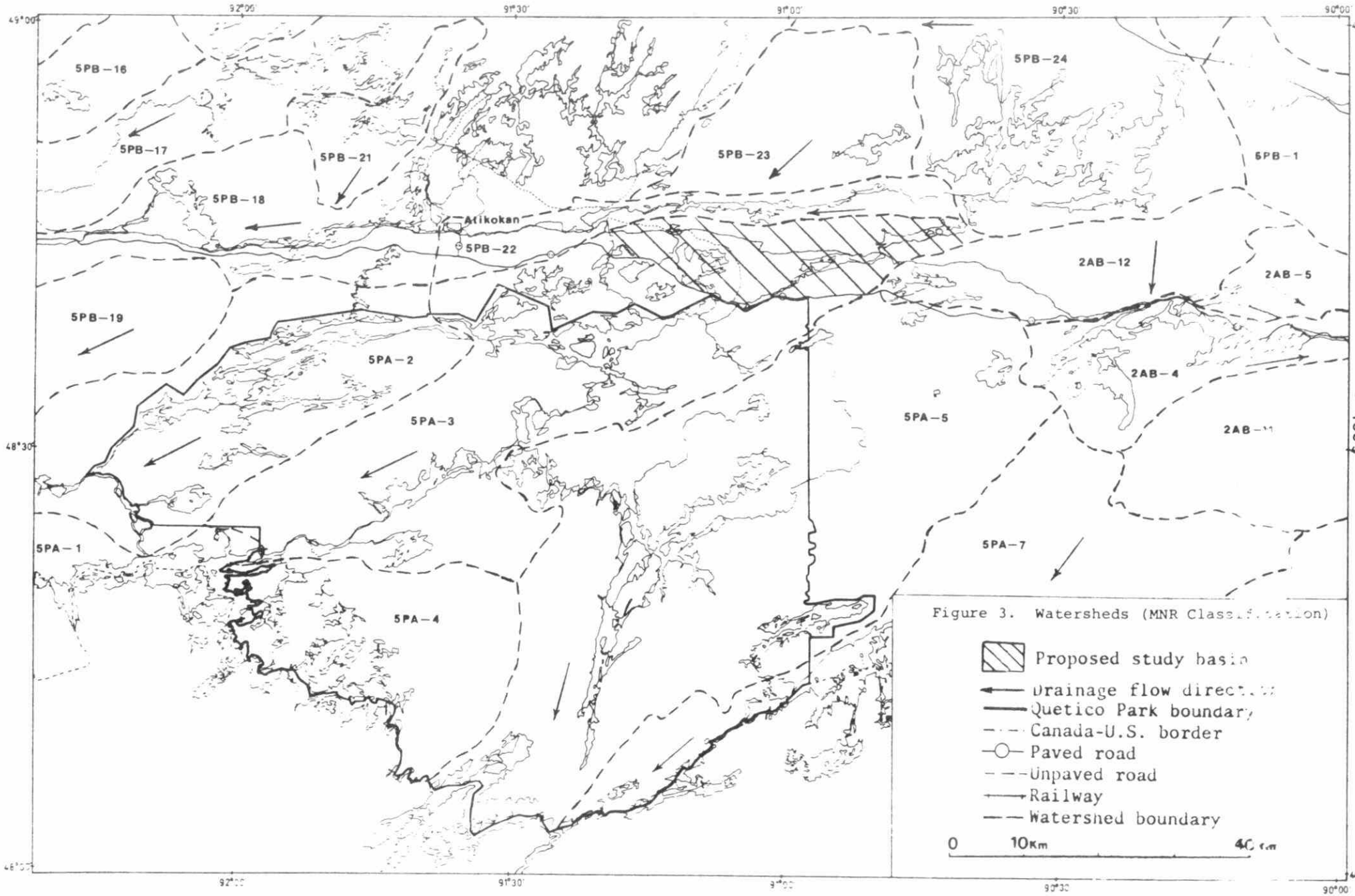


Figure 3. Watersheds (MNR Classification)

from 5.54 to 7.85. The field pH data are incomplete due to the malfunctioning of the portable digital pH meters part way through the study. The laboratory determined pH values range from 5.51 to 8.63. The average pH of the waters studied within Quetico Park is 6.59.

Chlorophyll a concentrations ranged from 0.00 to 11.40 mg/m^3, with an average value of 1.20 mg/m^3. The secchi depth varied from 1.5 to 7.5 m. The average is 3.6 m. These parameters have been used to define the trophic nature of lakes. In general, lakes exhibiting secchi depths of less than 3 m are eutrophic, while those with readings greater than 6 m are oligotrophic (Vallentyne, 1969). Using this criteria, only Elk (#14), Cone (#17), and Argo (#41) may be classified as oligotrophic, 57% of the lakes are mesotrophic, and 37% are eutrophic.

Chlorophyll a concentrations below 5 mg/m^3 are indicative of low to moderate algal densities characteristic of oligotrophic lakes, while concentrations greater than 10 mg/m^3 indicate high algal densities characteristic of eutrophic lakes (Michalski and Conroy, 1972). Of the 48 lakes for which chlorophyll a levels were determined, only 3 (6%), Omeme (#28), Unamed (#31), and Beaverhouse (#34), had levels greater than 5 mg/m^3. Of these, only Beaverhouse

had a level greater than 10 mg/m^3. The discrepancy between the results from the secchi depth classification and the chlorophyll a is undoubtedly due to the presence of humic and other particulate matter in the lakes.

Pheophytin levels ranged from 0.00 to 12 mg/m^3, with an average of 2.93 mg/m^3.

(b) Soil and Overburden

The location of the soil samples is shown on Figure 4. The sample number and its corresponding latitude and longitude is listed in Table 3. The results of the sediment size analysis is shown in Table 4.

Ground moraine is the most widespread glacial overburden in the study area. It is typically less than 1 m deep and is locally derived. The mineralogy of the overburden is reflected by the predominantly felsic intrusive and sediment derived gneisses which underly the area. The typical soil type formed from this parent material is a shallow (25 cm) podzol. The A horizon consists of approximately 1.5 cm of litter overlying a 6 cm zone of leached, tan-grey loamy sand. The B horizon is a tan-orange, medium size sand, approximately 7.5 cm thick. The C horizon is

Table 3. Soil Sample Locations

Map No.	Latitude	Longitude
1 s	48 38	91 30
2 s	48 42	91 20
3 s	48 38	91 48
4 s	48 33	92 00
5 s	48 40	91 14
6 s	48 43	91 14
7 s	48 41	91 53
8 s	48 42	91 55
9 s	48 44	92 15
10 s	48 48	92 28
11 s	48 53	92 26
12 s	48 37.5	90 12
13 s	48 39	90 18
14 s	48 40	90 58
15 s	48 52.5	91 12
16 s	48 43	91 35
17 s	48 51	91 45
18 s	48 55	92 02
19 s	48 53.5	91 57

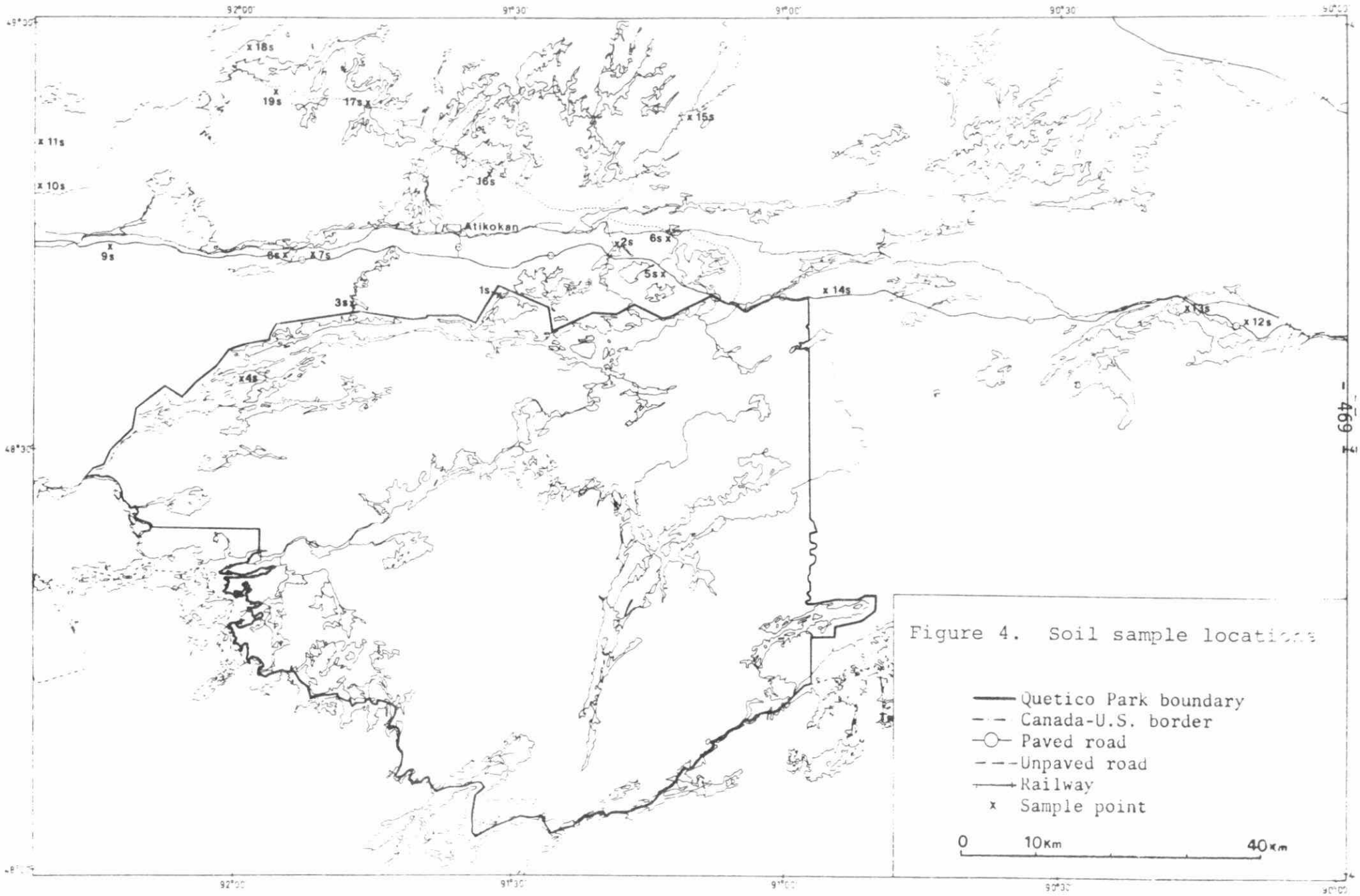


Figure 4. Soil sample locations

Table 4. Sediment Size Analysis

Map No.	Sample No.	Wt. % (retained-mesh size) 10	35	60	120	230	>230
1 s	78-B-3	52.75	17.35	11.18	11.65	4.66	2.41
2 s	78-B-4 A	67.18	25.72	3.25	1.20	0.88	1.75
2 s	78-B-4 B	0.45	15.20	37.86	26.92	9.79	9.77
3 s	78-B-5	0.63	2.04	3.98	13.77	45.57	34.01
4 s	78-B-6	3.32	9.86	26.06	41.00	14.03	5.73
5 s	78-B-7	42.86	42.13	5.66	2.92	1.54	4.89
6 s	78-B-8 A						
6 s	78-B-8 B	27.52	22.81	14.61	13.22	5.58	16.25
6 s	78-B-8 C	36.52	18.46	26.61	13.50	3.00	1.91
7 s	78-B-9						
8 s	78-B-11 A	0.36	7.79	33.58	37.41	12.25	8.60
8 s	78-B-11 B	0.90	7.14	31.79	36.83	14.40	8.95
9 s	78-B-12	-	16.15	49.51	23.50	6.45	4.39
10 s	78-B-13	-	-	-	-	-	100.00
11 s	78-B-14 A	0.99	63.06	27.69	2.79	0.92	4.55
11 s	78-B-14 B	3.08	59.25	29.92	3.19	0.99	3.56
11 s	78-B-14 C	2.85	2.70	3.43	23.18	38.75	29.08
12 s	78-K-9 B	14.81	31.57	32.67	15.39	3.48	2.09
12 s	78-K-9 C	6.78	82.78	10.43	-	-	-
12 s	78-K-9 D	-	0.11	2.32	55.34	29.63	12.61
13 s	78-K-11 B	0.45	15.20	37.86	26.92	9.79	9.77
13 s	78-K-11 C	0.63	2.04	3.98	13.77	45.57	34.01
14 s	78-K-19 B	0.19	55.79	30.37	6.94	2.79	3.92
15 s	78-K-31	-	0.01	0.16	3.43	16.73	79.67
16 s	78-K-42	2.34	6.24	12.55	26.15	21.12	31.59
17 s	78-K-49	4.43	6.35	20.32	37.59	17.47	13.84
18 s	78-K-56	-	0.12	5.26	48.65	26.93	19.04
19 s	78-K-60	20.10	37.02	29.22	9.42	2.28	1.96

typically a tan, medium grained sand, approximately 10 cm in thickness.

The results of the soil H^+-exchange capacity determinations are listed in Table 5 for the soil samples and some clay standards. It can be seen that the H^+-exchange capacities of the majority of the soil samples lie in the range of that shown by the kaolinite standard clay. Sample 78-K-9 D has an exchange capacity of 40.08 meq/100 gm over the pH range 7.56-4.98. This is much larger than the other samples and is due to the presence of $CaCO_3$. The exchange capacity is a function of the pH of the soil solution. This relationship can be seen since none of the soil solutions show a levelling-off in the amount of H^+ adsorbed per unit change in pH, at least down to pH 3.0. The pH-H^+ exchange capacity trend shows that saturation has not been reached by any of the samples. The exchange capacities listed in Table 5 are therefore not the total exchange capacities of the samples, but are the exchange capacities for the specified pH range.

(c) Precipitation

Water samples from 3 rain events were collected. The

Table 5. H^+-Exchange Capacity of Soil Samples and Standard Clays

Map No.	Sample No.	Soil pH	Ionic Strength NaCl x $CaCl_2$ o	pH range	H^+ exchange capacity meq/100 g
1 s	78-B-3	6.10	10^{-3} o	5.10-3.82	1.46
2 s	78-B-4 A	5.82	10^{-3} o	5.10-2.99	4.46
2 s	78-B-4 B	5.91	10^{-3} x	5.00-3.57	1.76
3 s	78-B-5	4.63	10^{-3} o	4.32-3.88	3.15
4 s	78-B-6	5.65	10^{-3} o	4.68-3.50	1.71
5 s	78-B-7	6.30	10^{-2} x	6.21-3.35	3.33
6 s	78-B-8 A	-	-	-	-
6 s	78-B-8 B	6.02	10^{-2} x	5.63-3.63	1.95
6 s	78-B-8 C	6.02	10^{-2} x	6.02-3.49	1.79
7 s	78-B-9	-	-	-	-
8 s	78-B-11 A	5.85	10^{-2} x	5.99-3.65	4.86
8 s	78-B-11 B	6.26	10^{-2} x	5.58-3.59	3.00
9 s	78-B-12	5.79	10^{-2} x	5.94-3.35	1.96
10 s	78-B-13	6.45	10^{-3} x	6.52-4.79	3.39
11 s	78-B-14 A	6.55	10^{-3} x	6.57-3.58	4.37
11 s	78-B-14 B	5.95	10^{-3} x	5.94-3.53	2.73
11 s	78-B-14 C	6.25	10^{-3} x	6.70-3.54	1.92
12 s	78-K-9 B	6.15	10^{-2} x	6.06-3.49	1.58
12 s	78-K-9 C	5.88	10^{-3} x	6.74-3.66	2.15
12 s	78-K-9 D	8.40	10^{-3} x	7.56-4.98	40.08
13 s	78-K-11 B	5.93	10^{-2} x	5.90-3.61	0.51
13 s	78-K-11 C	6.46	10^{-3} x	6.59-3.54	1.42
14 s	78-K-19 B	5.64	10^{-3} x	6.12-3.81	1.52
15 s	78-K-31	6.08	10^{-2} x	5.96-3.51	1.31

Table 5/continued

Map No.	Sample No.	Soil pH	Ionic strength NaCl x $CaCl_2$ o	pH range	H^+ exchange capacity meq/100 g
16 s	78-K-42	6.12	10^{-2} x	6.06-3.41	1.23
17 s	78-K-49	5.28	10^{-3} x	6.50-3.47	2.26
18 s	78-K-56	5.26	10^{-2} x	5.10-3.55	0.28
19 s	78-K-60	5.40	10^{-3} x	5.17-3.54	0.65
	Kaolinite #4		10^{-2} o	7.23-3.45	2.20
	Illite #35		10^{-3} o	7.23-2.69	20.61
Montmorillonite #22			10^{-3} o	8.26-3.29	34.51
	Quartz		10^{-2} x	4.88-3.48	0.04

pH ranged from 3.85 to 4.96 and the specific conductivity ranged from 8.0 to 20.5 μmho/cm.

IV. DISCUSSION

In the study area, dilute non-calcareous lakes are predominant. This is because the region is underlain by Precambrian bedrock and covered by a thin layer of unconsolidated glacial overburden derived from the bedrock.

In order to determine how well a lake assimilates H^+ without depressing the pH, the calcite saturation index (CSI) is calculated. The CSI is defined by:

$$CSI = pKI - pKC,$$

where $pKC = 8.02 + 0.0128\ t$,

t = temperature (°C), and

$pKI = 0.3 + 2pA + pK2 - pH$, where

$pA = -\log_{10}$ (Alkalinity, eq/ℓ), and

$pK_2 = 10.618 - 0.0115\ t$ (Kramer, 1977).

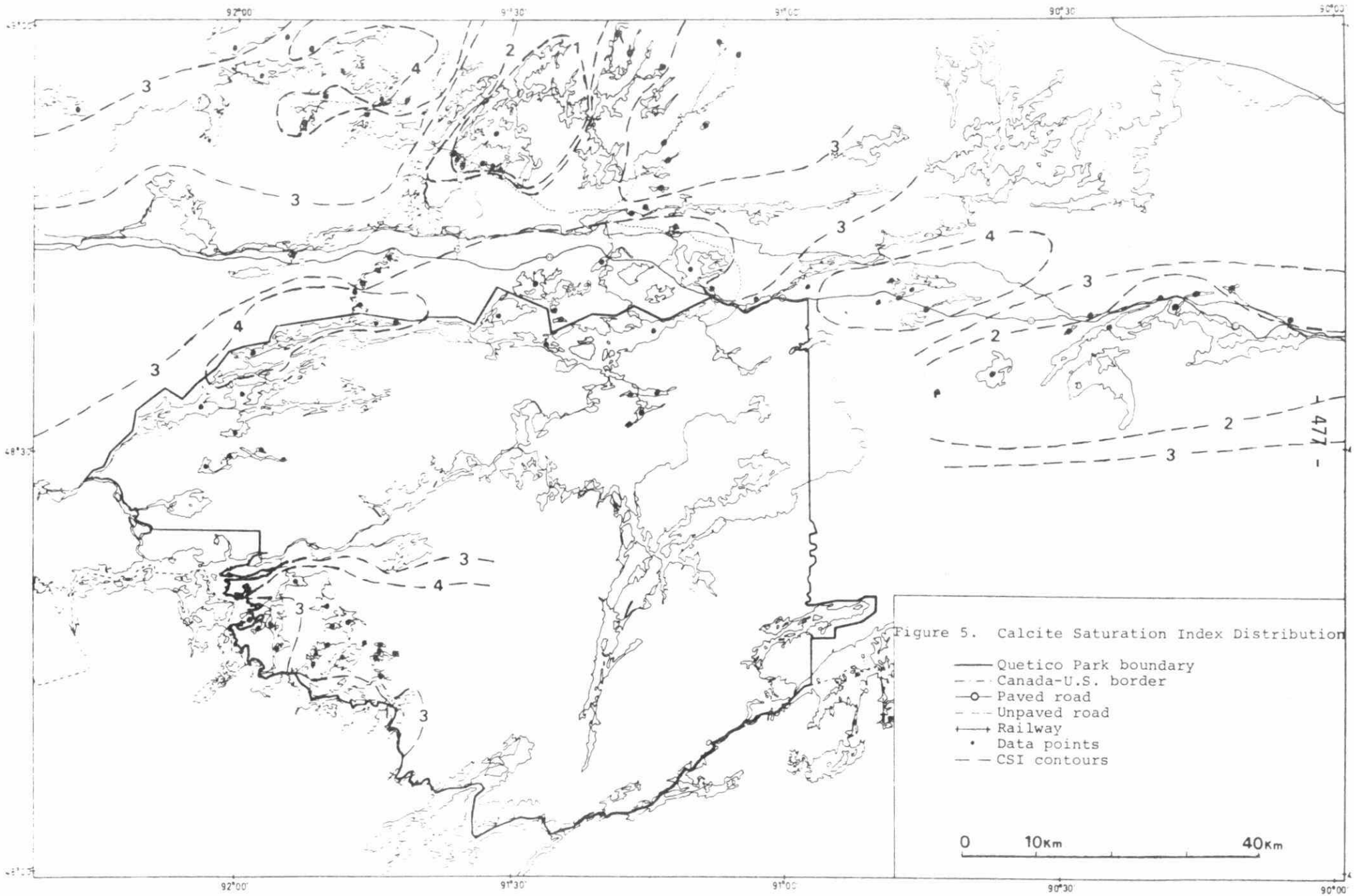
The CSI values for the water samples are listed in Table 6. Figure 5 is a plot of CSI for the study lakes. The CSI is positive for lakes of low H^+ assimilation capacity and approahces zero for saturation with respect to $CaCO_3$. Lakes with CSI values of 5-6 have virtually no assimilation capacity for H^+. Lakes with CSI values of 4-5 are highly susceptible to pH depression and continued H^+ loadings will affect lakes with CSI values of 3-4 in the future. A CSI value of 3 or greater is critical since 3 represents the CSI corresponding to the soil-water system with the minimum buffering and possibly the minimum exchange capacity (Malmer, 1976). A CSI of 3 also represents the point on the alkalinity-pH curve where the decrease in pH/alkalinity increases greatly. The susceptible portion of the area, as shown by CSI>3, is the hachured area shown in Figure 6.

Figure 7 is a plot of alkalinity vs. specific conductivity for the 101 water analyses. A linear least squares fit to the 101 samples is shown (solid line).

If one assumes that the ions contributing to specific conductivity are Ca^{2+} and HCO_3^-, and that the Onsager equation holds for a divalent-univalent system at low concentrations, then one may use the electroneutrality relationship, $2(Ca^{2+}) = (HCO_3^-)$, the equivalent ionic

Table 6. Calcite Saturation Index of Water Samples

Map No.	C.S.I.	Map No.	C.S.I.	Map No.	C.S.I.
1	3.01	36	3.95	72	2.93
2	3.44	37	3.69	73	2.42
3	3.71	38	3.85	74	3.65
4	2.55	39	3.77	75	3.70
5	3.12	40	4.03	76	3.57
6	2.80	41	3.61	77	3.19
7	4.37	42	3.35	78	2.54
8	4.14	43	3.50	79	3.01
9	3.51	44	2.34	80	3.30
10	5.60	45	2.34	81	0.89
11	4.00	46	3.23	82	1.94
12	3.28	47	3.70	83	2.09
13	3.61	48	3.64	84	3.32
14	3.22	49	3.88	85	0.55
15	3.26	50	4.20	86	2.53
16	3.55	51	3.62	87	1.57
17	3.33	52	5.49	88	0.57
18	3.44	53	3.99	89	0.96
19	2.29	54	4.31	90	-0.68
20	2.50	55	4.69	91	2.19
21	2.77	56	4.05	92	4.73
22	3.49	57	3.66	93	3.42
23	3.63	58	2.42	94	3.54
24	3.10	59	1.51	95	4.27
25	3.52	60	1.14	96	5.25
26	5.37	61	1.30	97	3.68
27	3.28	62	2.84	98	2.98
28	3.74	63	1.02	99	5.43
29	3.80	64	1.47	100	3.09
30	3.71	65	1.23	101	3.40
31	3.05	66	2.88	102	3.71
32	3.25	67	3.22	103	3.24
33	3.25	68	2.25	104	3.08
34	3.30	69	1.10		
35	2.64	70	1.46		


92°00'
91°30'
91°00'
90°30'
90°00'
48°30'
47°30'
1
2
3
4
Figure 5. Calcite Saturation Index Distribution
Quetico Park boundary
Canada-U.S. border
Paved road
Unpaved road
Railway
Data points
CSI contours
0
10Km
40Km

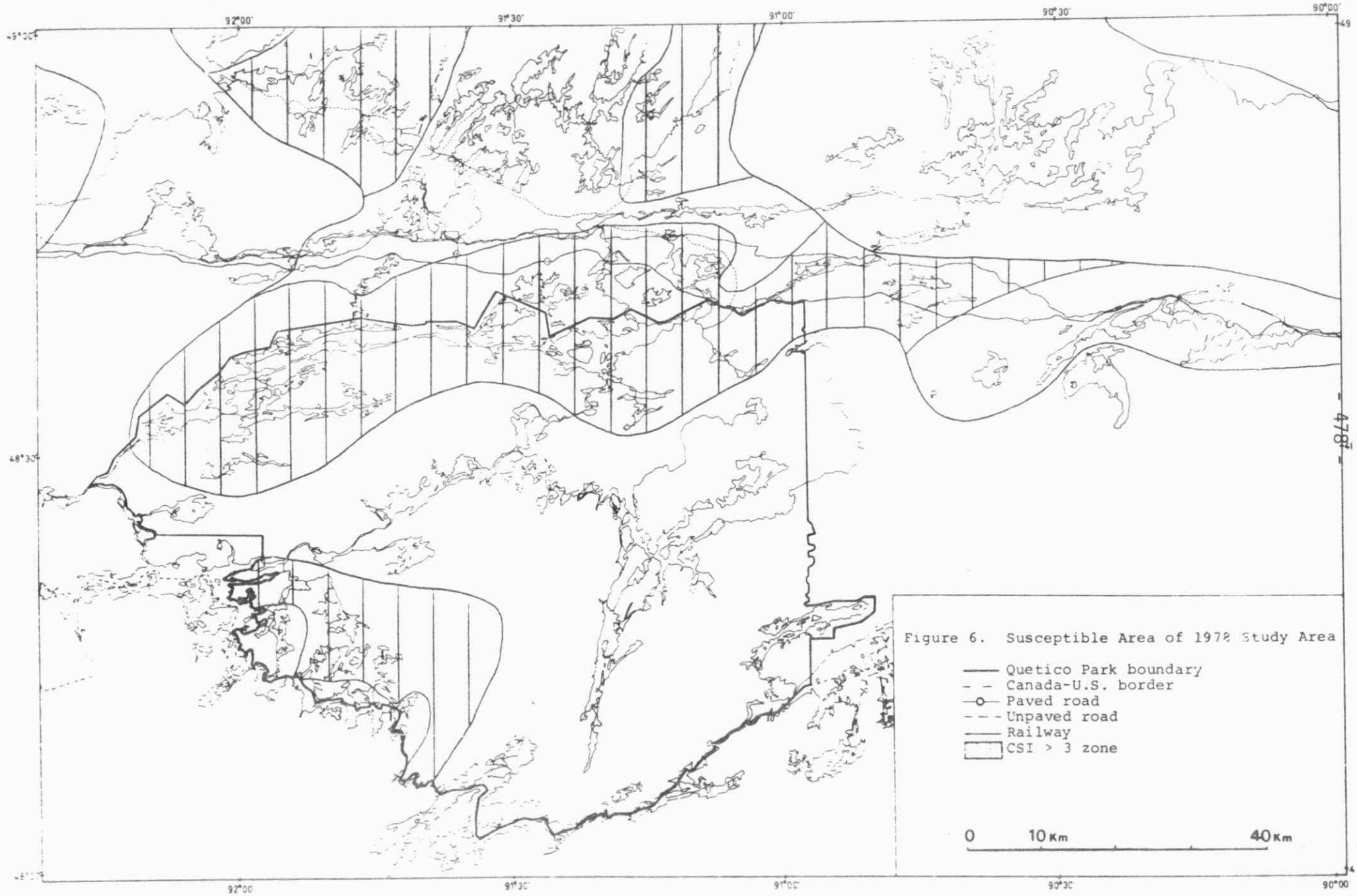
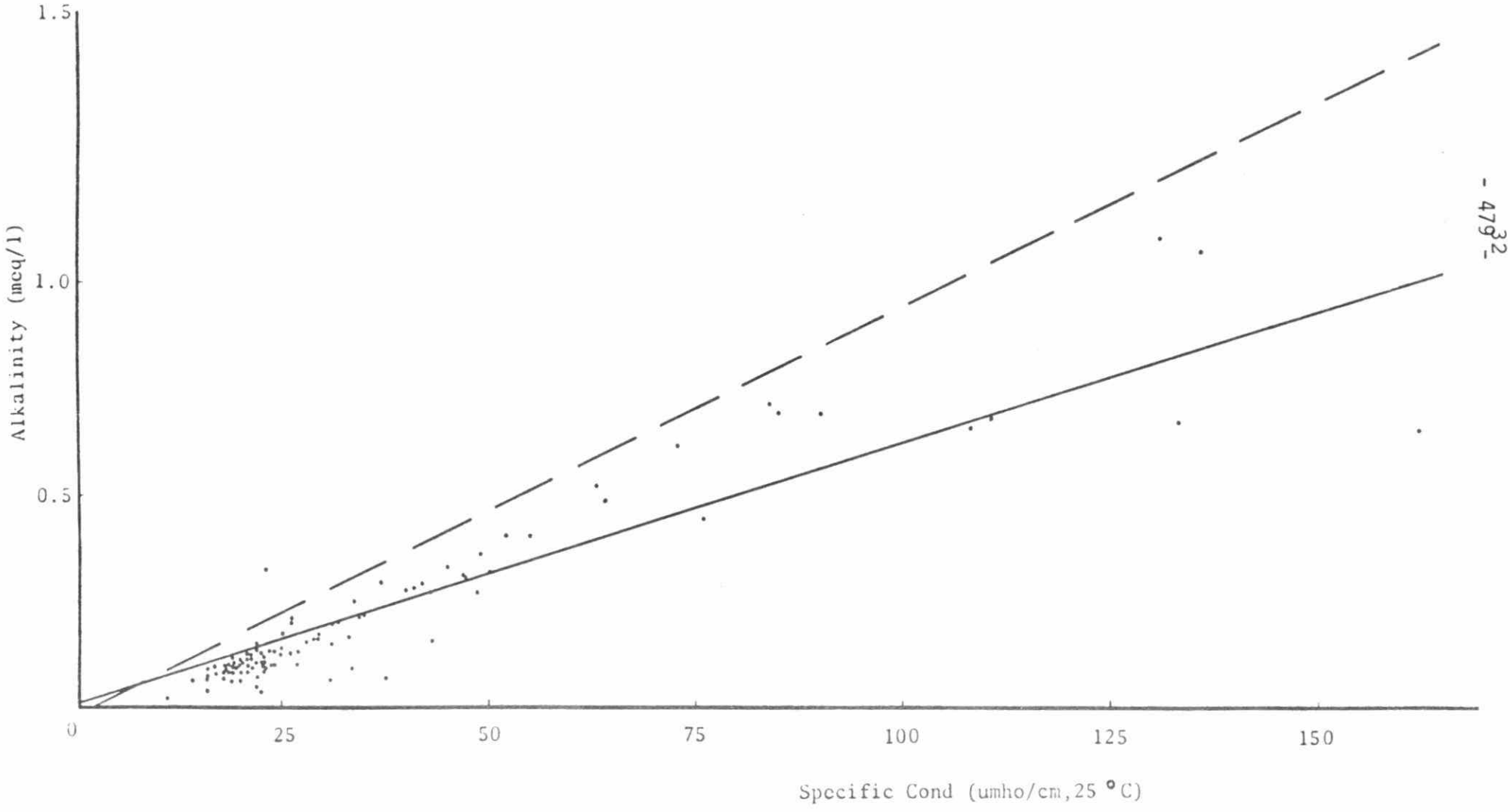

92°00'
91°30'
91°00'
90°30'
90°00'
49°00'
48°30'
Figure 6. Susceptible Area of 1978 Study Area
Quetico Park boundary
Canada-U.S. border
Paved road
Unpaved road
Railway
CSI > 3 zone
0
10 Km
40 Km

Figure 7. Relationship of specific conductivity and alkalinity of water samples

Alk=+0.00996 + .00617 Cond Lst Sqs(——) n=101 R=0.82

Alk=-0.012 + .00962 Cond Theoretical(– – –)



conductances for Ca^{2+} and HCO_3^- and substitute these into the Onsager equation. In the range of alkalinity of $0\text{-}2 \times 10^{-4}$ eq/ℓ, this equation has been found to simplify to:

Alk (meq/ℓ) = -0.012 + 0.00962 J (μmho/cm, 25°C) (Kramer, 1977).

This theoretical relationship is plotted on Figure 7 (dashed line). The theoretical and least squares lines are seen to fit fairly well with a correlation coefficient of 0.82. Since the data plot beneath the theoretical line by a fair amount, other ions are of significant concentration in addition to Ca^{2+} and HCO_3^-.

A plot of MNR specific conductivity versus the specific conductivity data of this study is shown in Figure 8. It can be seen that the data agree quite well, since most of the data points fall on or close to the line with slope equal to 1.0.

A plot of MNR alkalinity versus the alkalinity data of this study is shown in Figure 9. It can be seen from Figure 9 that the majority of the data points plot below the line with slope equal to 1.0. It appears that the method used by the MNR overestimates the alkalinity of the water samples, as compared to the method used in this study.

Figure 8. Comparison of MNR and this study specific conductivity measurements

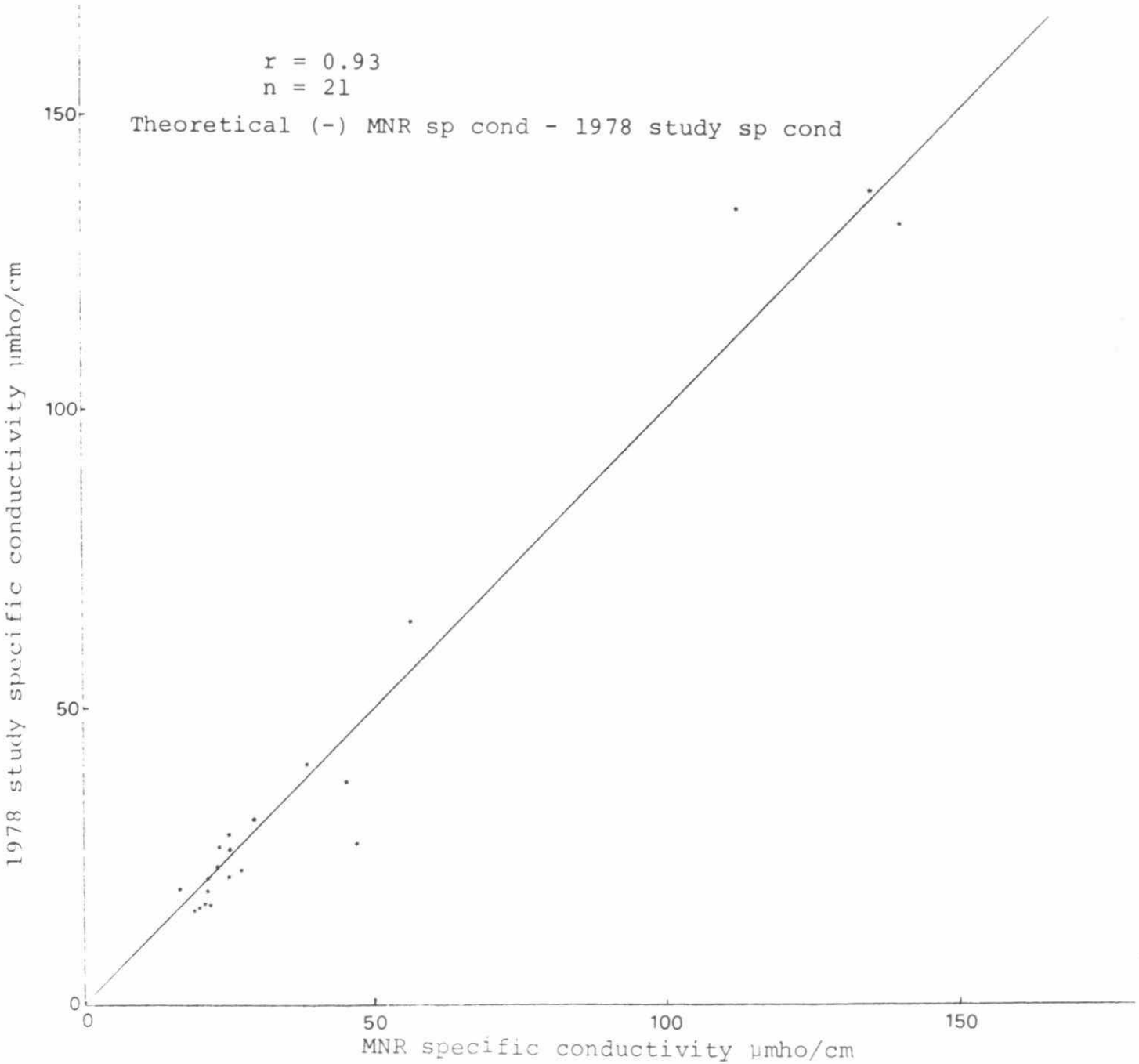
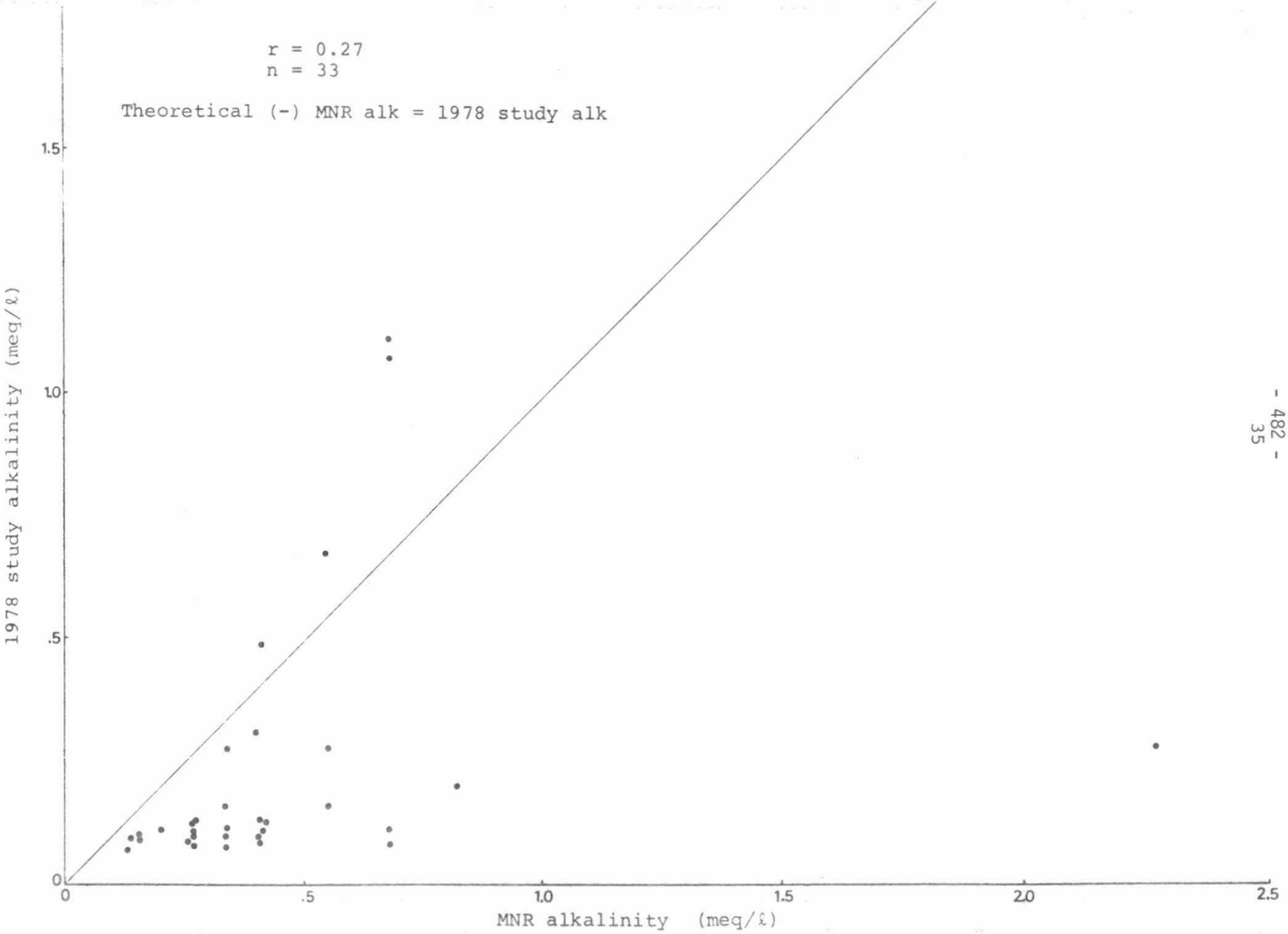
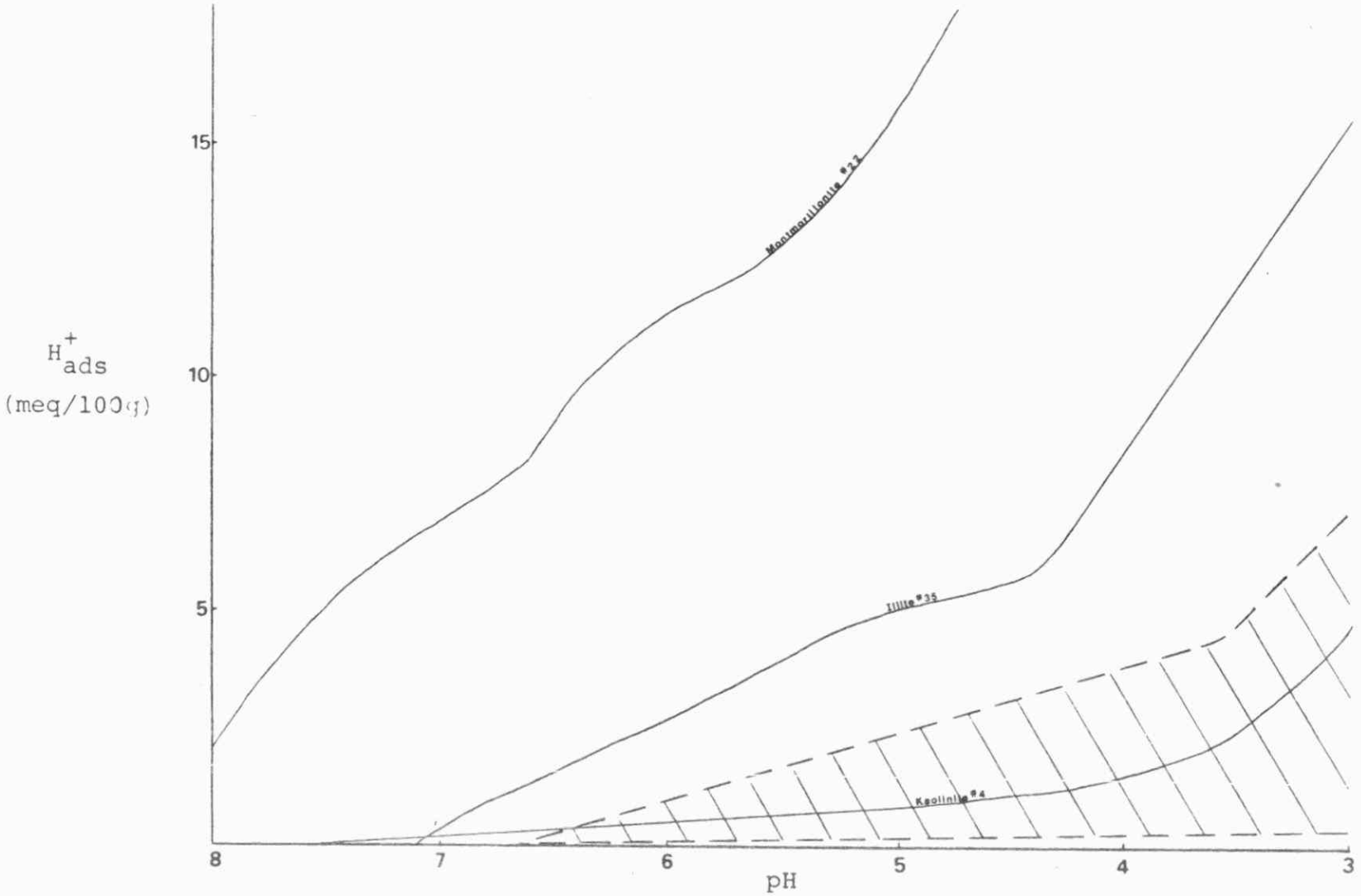


Figure 9. Comparison of MNR and this study alkalinity measurements



In a soil-water system, the major source of buffering capacity is the consolidated and unconsolidated soil and rocks. The exchange capacity (buffering) of these sediments is due mainly to the clay minerals and organics. Figure 10 is a plot of H^+ exchange capacity (meq/100 g) vs. solution pH for A.P.I. reference clays and the clay-size fraction of soils from this study. All samples show a nearly linear trend between H^+ capacity and pH down to a pH of approximately 4.5, and then an abrupt change in slope with increase in H^+ capacity. This change in slope may represent the beginning of the solution of the clay mineral. The field for the soil samples of this study is shown (hachured). The field occupies the lower portion of the plot which indicates that the soils of the study area are very poorly buffered. These soil pH-exchange relationships represent the ultimate capacity of the watershed. In order to predict trends in aquatic acidification of the area, this quantitative relationship between soil solution pH and H^+-exchange capacity of the soil is required. This may be used with a quantitative hydrologic model with surface runoff and soil infiltration which produces the flow relationships for reaction of acid precipitation with the soils.

Figure 10. H^+-exchange capacity vs. solution pH relationship for A.P.I. reference clays and clay size fraction of soils from this study (0.001 M $CaCl_2$ solution)



V. FUTURE WORK

A model of simultaneous solute and water transfer for an unsaturated soil is proposed in order to predict future trends in water quality. The natural soil system is modelled one-dimensionally from the surface to a stationary water table. The soil medium is assumed to be homogeneous.

The basic water flow equation for one-dimension is

$$\delta\theta/\delta t = -\delta v/\delta z \qquad (1)$$

where θ is the volumetric moisture content, t is time, z is depth measured positively downward, and v is the volumetric flux of water given by Darcy's law,

$$v = -K(\theta)(\delta H/\delta z) \qquad (2)$$

In (2), $K(\theta)$ is the unsaturated hydraulic conductivity expressed as a function of moisture content, and H is the hydraulic head defined by:

$$H = h - z \qquad (3)$$

where h is the pressure head.

Concentration variables θ, C, and S are combined to give the total amount of chemical in solution and on soil surfaces. Biological processes are ignored to simplify

the model. At any point in the soil the total amount of chemical is $\theta C + S$, which is increasing or decreasing with time. These changes must be due to:

(i) convergence of movement of the chemical toward the point or divergence away from the point and/or

(ii) a source or sink of the chemical at the point.

The second effect may be represented simply by "Q", which is positive for a source and negative for a sink. Figure 11 is a schematic of the flow system.

For a system containing two dominant cations, "a" and "b", the continuity equations are

$$\frac{\delta(\theta C_a + S_a)}{\delta t} = \frac{\delta}{\delta z}\left((K_{La} + D_a)\frac{\delta C_a}{\delta z}\right) - \frac{\delta(V_z C_a)}{\delta z} \pm Q_a \qquad (4)$$

$$\frac{\delta(\theta C_b + S_b)}{\delta t} = \frac{\delta}{\delta z}\left((K_{Lb} + D_b)\frac{\delta C_b}{\delta z}\right) - \frac{\delta(V_z C_b)}{\delta z} \pm Q_b \qquad (5)$$

The notation for describing the movement is defined in Table 7.

Table 7. Flow Model Notation

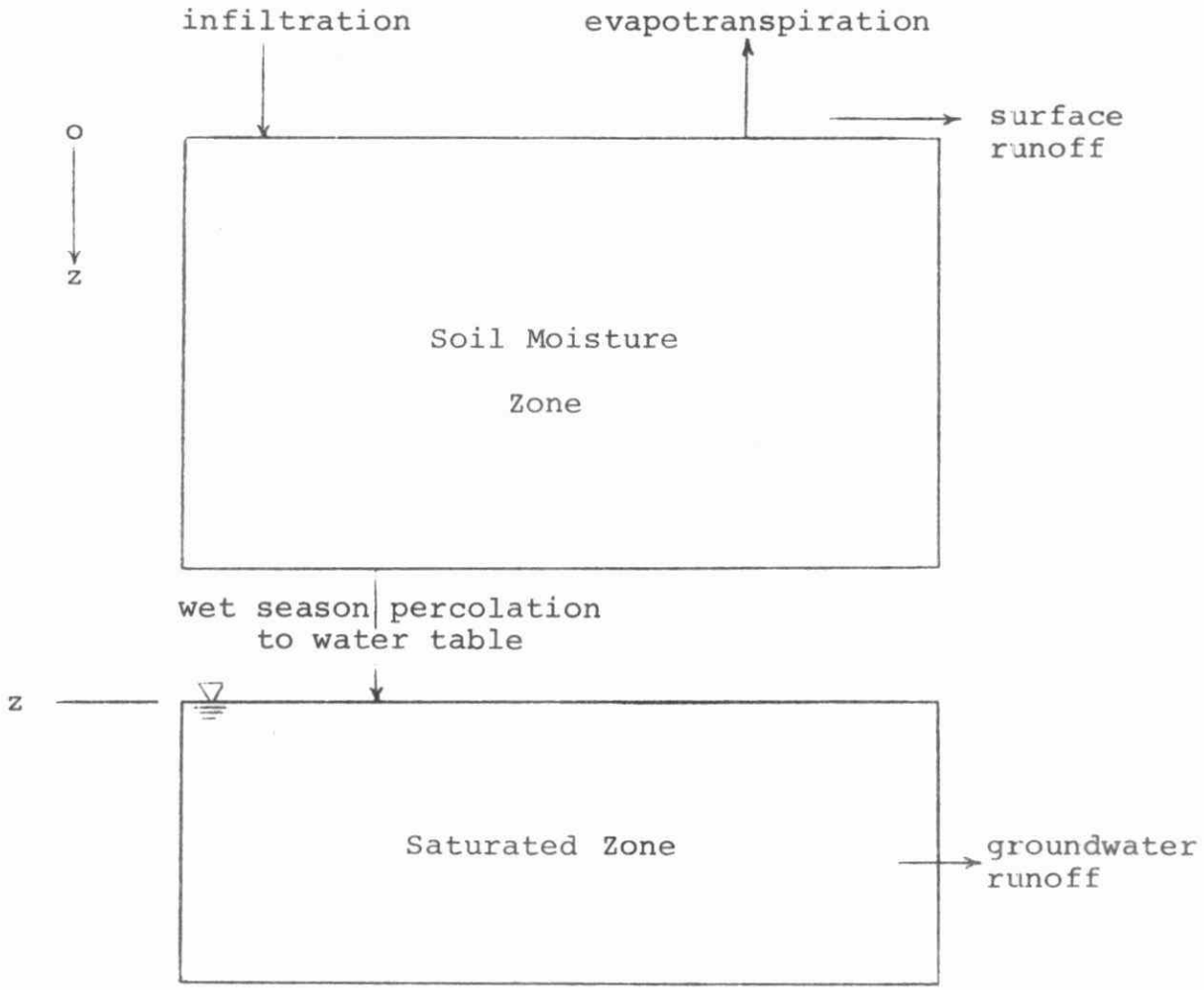
Symbol	Definition	Dimensions
z	space coordinate	L
t	time coordinate	T
θ	effective volumetric moisture content	L^3/L^3
C	solution concentration of chemical	M/L^3
K_L	longitudinal dispersion coefficient	L^2/T
S	amount of chemical adsorbed on soil surfaces	M/L^3
V_z	rate of movement of water in the z direction per unit area perpendicular to the direction	L^3/L^2T
D	molecular diffusion coefficient	L^2/T
Q	rate of supply or loss of chemical per unit volume	M/L^3T

The first term on the right-hand side of equations 4 and 5 describes the movement of the chemical due to molecular diffusion and hydrodynamic dispersion. Since hydrodynamic dispersion and molecular diffusion are represented by equations of the same form

$$\text{Molecular diffusion} = -D\delta C/\delta z \quad \text{(Fick's Law)} \qquad (6)$$

$$\text{Dispersion} = -K_L \delta C/\delta z \quad \text{(proportionality law)} \qquad (7)$$

Figure 11. Flow Model



they become mathematically indistinguishable and their effects can be added. The combination may be referred to as the apparent diffusion. The diffusion coefficient D and the dispersion coefficient K_L may be replaced by the apparent diffusion coefficient, D_K. Equations 4 and 5 can be rewritten as

$$\frac{\delta(\theta C_a + S_a)}{\delta t} = \frac{\delta}{\delta z}(\theta D_K \frac{\delta C_a}{\delta z}) - \frac{\delta(V_z C_a)}{\delta z} \pm Q_a \qquad (8)$$

$$\frac{\delta(\theta C_b + S_b)}{\delta t} = \frac{\delta}{\delta z}(\theta D_K \frac{\delta C_b}{\delta z}) - \frac{\delta(V_z C_b)}{\delta z} \pm Q_b \qquad (9)$$

The second term on the right-hand side of equations 8 and 9 describes the movement of the chemical due to simple convection or piston flow.

Since there are four unknowns, C_a, C_b, S_a, and S_b, four simultaneous equations must be solved. The first two are equations 8 and 9. The third is the adsorption equation. An example is the Freundlich competition between ions "a" and "b" $\delta S_a/\delta t = K_1 (C_a S_b - \frac{1}{K_2} S_a C_b)$ (10) for a non-equilibrium condition.

For many soils the mono-divalent exchange equilibrium may be described by the expression:

$$\frac{S_a^+}{S_b^{2+}} = K_G \cdot \frac{C_{a+}}{\sqrt{C_b^{2+}}/2} \qquad (11)$$

However, the above relationship may not hold well at low pH for H^+, since it enters into the clay lattice displacing a structural ion such as Al.

If the dominant complementary cation on the exchange complex with H^+ is Ca^{2+}, then slightly acidic soils (pH 5-7) will tend to be buffered with respect to both Ca-ions and H^+-ions. The ratio law states that if a soil is in equilibrium with a solution of a given composition in Ca and H, it is also in equilibrium with all other solution compositions in which $a_H/\sqrt{a_{Ca}}$ has the same value as in the original equilibrium solution. Consequently, the composition of the equilibrium solution of the slightly acidic soil may be characterized by a particular value of $a_H/\sqrt{a_{Ca}}$ which is constant with small changes in ionic strength due to the addition of salts and/or dilution with water. The negative logarithm of the above activity ratio is $(pH - \frac{1}{2}\, pCa)$, and this term has been called the 'lime potential'. As compared to the pH of a soil, which for a given composition of the exchange complex with respect to H^+ and Ca^{2+} ions is still quite variable with total electrolyte level or moisture content, the lime potential is more constant. It is

consequently a better characteristic of the exchange complex with respect to H^+/Ca^{2+}. An adsorption equation of the form

$$\frac{S_a^+}{S_b^{2+}} = a + b\ (pC_{a+} - \frac{1}{2}\ pC_{b2+}) \qquad (12)$$

is currently being investigated for soils collected in the 1978 study area.

The fourth equation

$$S_a + S_b = C.E.C. \qquad (13)$$

is the relation describing the exchange capacity which is available to the two chemicals "a" and "b".

The value of D_K is a function of the pore water velocity distribution. Its value depends on the average water flow velocity and the soil moisture content. If D_K is assumed constant and (1) is used, (8) and (9) become

$$\frac{\delta C_a}{\delta t} + \frac{1}{\theta}\frac{\delta S_a}{\delta t} = D_K\frac{\delta^2 C_a}{\delta z^2} - \left(\frac{V}{\theta} - \frac{D}{\theta}\frac{\delta\theta}{\delta z}\right)\frac{\delta C_a}{\delta z} \pm Q_a \qquad (14)$$

$$\frac{\delta C_b}{\delta t} + \frac{1}{\theta}\frac{\delta S_b}{\delta t} = D_K\frac{\delta^2 C_b}{\delta z^2} - \left(\frac{V}{\theta} - \frac{D}{\theta}\frac{\delta\theta}{\delta z}\right)\frac{\delta C_b}{\delta z} \pm Q_b \qquad (15)$$

where "Q_a" and "Q_b" are the source-sink terms.

The boundary and initial conditions for $\theta(z,t)$ and $C(z,t)$ for infiltration with a slug of water containing solutes of concentration $C_{o,a}$ and $C_{o,b}$ are

$$\theta(z,0) = f(z) \tag{16}$$

$$\theta(0,t) = \theta_{wet} \qquad t < t_1 \tag{17a}$$

$$\theta(0,t) = 0 \qquad t > t_1 \tag{17b}$$

$$C_a(z,0) = C_1 \tag{18a}$$

$$C_b(z,0) = C_2 \tag{18b}$$

$$C_a(0,t) = C_{o,a} \qquad 0 < t < t_1 \tag{19a}$$

$$C_b(0,t) = C_{o,b} \qquad 0 < t < t_1 \tag{19b}$$

$$C_a(0,t) = 0 \qquad t > t_1 \tag{20a}$$

$$C_b(0,t) = 0 \qquad t > t_1 \tag{20b}$$

$$S_a(z,0) = S_1 \tag{21a}$$

$$S_b(z,0) = S_2 \tag{21b}$$

The initial moisture content distribution within the soil profile is assumed arbitrary (equation 16). The initial solute concentrations are also assumed arbitrary (18a and 18b). The value t_1 is the time required for total infiltration of the surface water. At the soil-atmosphere interface, the boundary conditions are as follows:

For infiltration

$$i_r = i_c \qquad s_o = 1 \qquad p > i_c$$

$$i_r = p \qquad s_o < 1 \qquad p < i_c$$

For exfiltration

$$e_r = E_T = e_c \qquad s_o = 0 \qquad E_p > e_c$$

$$e_r = E_T = E_p \qquad s_o > 0 \qquad E_p > e_c$$

where s_z is defined as the effective degree of medium saturation (θ/n), (i.e. s_o as the degree of saturation at the surface, $z = 0$), i_r as the infiltration rate, i_c as the infiltration capacity, p as the rainfall rate, E_T as the actual evaporation rate, and E_p as the potential (soil surface) evaporation rate. Since for $p < i_c$ and for $E_p < e_c$ the actual moisture exchange rates are fixed by the climatic variables p and E_p respectively, the soil moisture equations are solved for one infiltration condition (saturated surface) and one exfiltration condition (dry surface).

The difference between p and i_c, where $p > i_c$ is surface runoff (S_r).

The transfer of water and solutes from the unsaturated zone to the saturated zone is described by the apparent percolation velocity $\underline{V}$ which is assumed to be a steady gravitational seepage:

$$V = K(\theta = ns_z) = K(s_z)$$

where ns_z is the soil moisture at the lower extremity of the soil moisture zone.

A finite difference solution of (1) can be used to determine values of V(z,t) and these are used to solve the continuity equations. A method used to solve equation (1) has been given by Hanks and Bowers (1962). The method requires, in addition to knowledge of the initial and boundary conditions:

(a) A known relation between moisture content and pressure head;

(b) A known relation between moisture content and moisture diffusivity.

The method does not require that:

(a) The soil be homogeneous throughout;

(b) The soil be semi-infinite;

(c) Gravity be neglected;

(d) That the initial moisture content be uniform.

The proposed study area to which the above model may be applied is shown in Figure 3 (hachured).

Initial work in the study area would involve the determination of the physical and chemical soil parameters. This would include the determination of a characteristic

soil profile for the area. An experimental plot will be required for calibration and verification of the infiltration model. Representative soil columns from the study area will be obtained in order to experimentally determine the following parameters:

(i) soil porosity (θ)

(ii) soil conductivity $K(\theta)$

(iii) soil diffusivity $D(\theta)$

(iv) soil water pressure $H(\theta)$

(v) initial soil chemistry (S_a, S_b $(z,0)$) and the H^+_{ads} *vs.* $(pH - \frac{1}{2}pCa)$ relationships.

Soil water samplers will be installed at various depths to establish initial values for $C_a(z,0)$ and $C_b(z,0)$ and to monitor changes in these with respect to time.

In order to be able to predict the chemistry and flow of the two streams leaving the study basin, the relative magnitude of the main components of stream runoff: (i) direct runoff, (ii) interflow, and (iii) base flow, must be determined for the study basin terrain. Direct runoff occurs only during and immediately after a rainfall event. It is due to rain falling on either a saturated or impervious surface. Therefore, the percentage of the study

area which is impervious to infiltration (i.e. exposed bedrock) must be determined.

In order to be able to determine base flow, the average depth of the groundwater aquifers and their spatial distribution must be determined along with the basic physical parameters (groundwater slope and aquifer permeability). Changes in concentration over time due to the processes of convective transport, hydrodynamic dispersion, and mixing (or dilution) may be determined by using a computer model such as that of Konikow and Bredehoeft (1978). The model assumes that there is no reaction between the solute and the aquifer material.

In order to calibrate the model, the two streams leaving the watershed must be gauged and samples of water collected for chemical analysis on a regular schedule.

The precipitation data may be obtained from the nearest government sampling station, i.e. Atikokan and/or from samplers set up in the study area. The model should be run for one full year of precipitation data for verification of the flow. Verification of the chemical portion of the model is more difficult since approximately 10 years of precipitation is probably required in order for a significant, measurable change in soil and soil water to occur.

REFERENCES

EAGLESON, P.S., 1978. Climate, soil, and vegetation. 3. A simplified model of soil moisture movement in the liquid phase. Water Resources Research, 14, 5, 722-729.

HANKS, R.J. and S.A. BOWERS, 1962. Numerical solution of the moisture flow equation for infiltration into layered soils. Soil Sci. Soc. Amer. Proc., 26, 530-534.

KONIKOW, L.F. and J.D. BREDEHOEFT, 1978. Computer model of two-dimensional solute transport and dispersion in ground water. Techniques of Water Resources Investigations of the U.S. Geological Survey, Book 7, Chapter C2.

KRAMER, J.R., 1977. Geochemical factors and terrain response to environmental factors. Dept. Geology, McMaster Univ., report to Inland Waters Directorate Research Subvention Program, Ottawa, 1-30.

KRAMER, J.R., 1976. Assessment of the ecological effects of long-term atmospheric material deposition. Applied Earth Sci. Consultants, report to Environment Canada, Federal Activities Branch, Ottawa, 83p.

MALMER, N., 1976. Acid precipitation: chemical changes in the soil. Ambio, 5, 231-234.

MICHALSKI, M.F.P. and N. CONROY, 1972. Water quality evaluation, Lake Alert Study, Ontario. Ministry of the Environment, Water Quality Branch, 23p.

VALENTYNE, J.R., 1969. Process of eutrophication and criteria for trophic state determination. In Modelling and Eutrophication Processes. Proc. of Workshop, St. Petersburg, Fla., Nov. 19-21, 57-67.

WARWICK, A.W., J.W. BIGGAR and D.R. NIELSEN, 1971. Simultaneous solute and water transfer for an unsaturated soil. Water Resources Research, 7, 5, 1216-1225.

ZOLTAI, S.C., 1965. Glacial features of the Quetico-Nipigon area. Can. Jour. Earth Sci., 2, 3, 247-269.

PART 2.

Aluminum in water: preliminary results

Summary: 50 ml samples collected in polyethylene are buffered to pH 5, lumogallion reagent added, and sample digested in heat bath. Fluoresecnce of the compound is measured using a Turner fluorometer model #111, excitation wavelength 465 nm, emission wavelength 555 nm, and a flow through system. Standard additions are made on all results due to interferences from Mn and humic acid.

Introduction:

There has been recent concern regarding the role of Al as a toxicant in acidic water (1). Clay minerals and other alumino-silicates release Al in measurable amounts below a pH of 5-6, and they become increasingly more soluble at even lower pH's. For most reported results to date, the Al values follow no dissolution model. Furthermore it is not clear what form(s) of Al are toxic. Before these questions and related questions can be answered, a reliable method for analysis of aluminum must be developed.

Studies reporting Al in soft waters have used colorimetric techniques, either the catechol procedure (2), or the Ferron procedure (3). Both have marked interferences from other metals, specifically Fe and Mn, and modifications in these techniques to suppress the effect of these interferences are carried out. However, as will be reported further, these modifications must be considered suspect. As a matter of fact, all methods of analysis must be considered subject to interference because of the atomic and ionic nature of the group of elements being considered. They are all highly reactive with a large number of substances. The greatest care using standard addition technique

routinely must be exercised.

The method used here depends upon the fluorescence of Al and lumogallion. This method is basically that of Hydes and Liss (4). This method has fewer potential interferences than any of the colorimetric methods, but it is affect by high concentrations of Fe(+3), Mn, and humic acid. Therefore standard addition technique is used routinely.

In brief, samples are collected in polyethylene or polypropylene containers; 50 ml samples are buffered to pH 5, lumogallion reagent is added and allowed to react with dissolved aluminum. The fluorescence of the compound is measured using a Turner #111 fluorometer, excitation wavelength 465 nm, emission wavelength 555 nm, and a flow through cell door. The digestion was carried out manually, and measurements were made using an auto-analyser pump, Gilson sampler changer, and Turner #111 fluorometer.

Sample bottles: 125ml wide-mouthed polypropylene bottles are soaked overnight in 10% HNO_3. The bottles are also stored in HNO_3 solution. HCl is not recommended as it is normally contaminated either due to a basic Al impurity or leaching from the glass container. Probably Al-Cl complexes are formed with HCl but not with HNO_3.

Reagents: Lumogallion- 0.02 % w/v in deionized water. Stable 1 month. Buffer- Sodium acetate trihydrate solution brought to a pH of 8 and filtered through 0.45 um paper. Then brought to a pH of 5 with aristar acetic acid. Final solution concentration is about 4 molar. Al standard- Aluminum potassium sulfate--1.758 g/loo ml (1000 ppm standard). It is stable 3 weeks. Acid soaked volumetrics are used in the preparation of standards and the lumogallion solution. When making secondary standard solutions

for standard additions, dilutions are carried out gravimetrically in polupropylene containers, and the solutions are kept at a pH of 1 by addition of a few drops of concentrated Aristar HNO_3. Standard additions are made using micropipets. The maximum standard addition was kept to less than one-half the expected value of the sample.

Detection limit: The lower limit of detection is 0.5 ppb using the flow-through door. With a lumogallion concentration of 2 mg/L, the calibration curve is linear up to 120 ppb Al. Typically dilutions are made so as to work in the 10-20 ppb range. A sample wash of 0.01 N HNO_3 is used to keep glassware from adsorbing Al.

Method: More consistent results were obtained if samples were filtered through 0.45 um Millipore paper before analyzing. The sinter and the paper must be washed with HNO_3, and the filter sinter is kept soaking in 10% HNO_3. 50 mL of sample are measured into a polypropylene bottle gravimetrically, and appropriate standard additions are made. 0.5 mL of lumogallion are added using a micropipet, and 0.5 mL of buffer solution are added. SAmples are shaken, heated in a hot water bath at 80°C for 1-1/2 hours, and cooled to room temperature. Samples are transferred to poylpropylene test tubes which have been soaked with HNO_3, placed in a Gilson sample tray, and covered with a plastic sheet to keep out room dust. Samples are pumped at 3.4 mL/min, and the same flow is used for waste. A 0.8 mL/min debubbler flow is used. Sample time is 3 min and wash time is 3.5 min. For a typical analysis, sample with and without lumogallion, and samples with 1.1, 1.2 and 1.5 times expected value are run.

Fe interference: A 50 ml sample of 200 ppb Al with 2 mg/L (0.5 mL) lumogallion were given additions of 25,50, and 100 ppb Fe:

The apparent Al concentrations are:

20 ppb Al +	25 ppb Fe	give	20 ± 0.08* ppb Al
	50		22.1 ± 0.11 ppb Al
	100		16.5 ± 0.55 ppb Al

* ± values are one standard deviation for 5 runs. Expected standard deviation for a simple Al solution at this concentration for 5 sample replication is 0.03. Increasing the lumogallion concentration to 2.8 mg/L improves the measurement so that 50 ppb addition of Fe produces an apparent 20.5 ppb Al, and a 100 ppb addition of Fe produces an apparent 19 ppb Al. Hydes and Liss (4) found that 50 ppb addition of Fe did not affect their readings but there appears to be a slight enhancement in the apparent Al concentration from this study.

Effect of Mn : Mn(+2) was added to a 2 ppb Al solution. The apparent Al due to addition is:

2 ppb Al +	2 ppb Mn	gives	4.6 ppb apparent Al
	5		4.6
	10		20 +

This was an early experiment, and the quantitative relationship may be unreliable, but it is certain that 10 ppb Mn greatly increases the apparent Al concentration.

Humic acid experiments: A 20 ppb solution of Al (+ 0.5 ml lumogallion) were given addiiton of 5 and 0.5 ppm humic acid (HA - Aldrich Chemical Company):

20 ppb Al +	5 ppm HA	gives	37.6 ± 1 ppb apparent Al
	0.5		21

Irradiation experiments were carried out to suppress the HA affect; Samples were placed in 10% HNO_3 soaked quartz test tubes surrounding an ultra-violet radiation tube and the samples were irradiated for 1 hr.

	before irradiation	after UV	
5 ppm HA + 2 mg/L lumo.	19.5	16.3	apparent
1 ppm Ha + 2 mg/L lumo.	5.8	2.8	Al (ppb)
5 ppm Ha and no lumo.	3.3	--	
5 ppm HA + 2 mg/L lumo. + 20 ppb Al	36.4	36.3	

0.5 ppm HA does not affect the apparent Al concentration, but 5 ppm HA has a marked increase in the apparent Al concentration. Irradiation for 1 hr does not help. 5 ppm HA has a natural fluorescence of about 3.3 ppb Al equivalence in the analystical set-up.

Analysis of some samples: Samples were kindly collected by N Conroy and W. Keller of the Ontario M.O.E. from soft water lakes In addition samples of Lake Ontario were analysed. Lake Ontario samples resulted in a concentration below a detection limit of 0.5 ppb Al. All samples were analysed using a standard addition technique. In addition high concentration samples were diluted to less than 20 ppb. The results are:

	George L.	Clearwater L.	Onaping L.	?
pH	5.14	4.21	6.46	5.50
Al(ppb) 0.45 um filtered:	46.9	429	9.29	74
ultra-filt. UM05	30	144		

No samples exhibited natural fluorescence. The results for the ultrafiltered samples were more noisy suggesting contamination in the filtering system.

Interpretation of results:

Although there are only a few numbers available to interpret, they do represent extremes in pH. Converting the 0.45um filtered results in the preceding table to molar units, there is an approximate change of the log(10) of the concentration of Al and H^+ of a slope of about 0.7, or:

$$p\ (Al) = 2.2 + 0.7\ pH$$

It is worthwhile to see if any of the common dissolution reactions has a similar slope.

The alumino-silicates, Ca-feldspar, Na-K feldspars, kaolinite, and gibbsite etc are often suggested as sources of weathering and release of Al to solution. Stoichiometries involved in their solution are:

K-Na feldspar:

$$4\ H_2O + K,Na)AlSi_3O_8 + 4\ H^+ = Al^{+3} + K,Na^+ + 3\ H_4SiO_4$$

for a congruent solution:

one obatains: $p(Al) = K + pH$, or at equilibrium

$$p(Al) = 1.34 + pH$$

Ca-feldspar:

$$CaAl_2Si_2O_8 + 8\ H^+ = 2\ Al^{+3} + Ca^{+2} + 2\ H_4SiO_4$$

or, $$p(Al) = k + 8/5\ pH$$

Kaolinite:

$$0.5\ Al_2Si_2O_5(OH)_4 + 3\ H^+ = Al^{+3} + H_4SiO_4 + 0.5\ H_2O$$

or $$p(Al) = k + 1.5\ pH$$

mucovite:

$$KAl_3Si_3O_{10}(OH)_2 + 10\ H^+ = 2\ Al^{+3} + 3\ H_4SiO_4 + K^+$$

or $$p(Al) = k + 10/7\ pH$$

In the above, K and k are constants explicit to each reaction. The important point is to note that the slope of log Al to log H is consitently much different than any of the reactions (pH/pAl for actual measurements = 0.7 whereas mineral solution stoichiometries are greater than 1). Either these are not the proper reactions, or the consideration is much too simplified (congruent solution). It is apparent that other measurements including Si must be carried out. Furthermore examination of the surfaces of weathered alumino-silicates in the acid lakes must be examined to determine what the reactive phases releasing Al are.

NB. This is an initial summary of results and interpretation on the analysis, geochemistry and toxicity of Al and associated materials in an aquatic environment.

References

1) Burrows, W.D. (1977) Auquatic aluminum chemistry toxicology and environmental prevalence. Critical Reviews in environmental control, p. 167-216.

2) Dougan, W.K. and A.L. Wilson (1974) Analyst, 99, p. 413-430.

3) Brown, E., M.W. Skougstad, and M.J. Fishman (1970) Methods for collection and analysis of water samples from dissolved minerals and gases. U.S. Geological Survey, Book 5, Chap. A1. in Techniques of water resources investigations of the United States Geological Survey, p. 44-46.

4) Hydes, D.J. and P.S. Liss (1976) Analyst, 101, p. 922-931.

PART 3.

ALKALINITY MEASUREMENTS IN SOFT WATERS

Alkalinity is defined as the number of H^+ ions consumed relative to a defined chemical system and an equivalence point in that system. A typical example in a general sense is: Imagine a "weak" acid of H^+, ligand L, and undissociated HL: Then $HL = H^+ + L^-$

If we start with L>HL and we add H^+, we consume H^+ by forming HL; when L gets small from addition of and reaction with H^+, there remains more and more free H^+; finally a point is reached where H^+ concentration is equal to L concentration. This is the equivalence point. Beyond this equivalence point, HL>L. Now imagine instead of one ligand,L, many ligands, L_1, L_2 ... There are various equivalence points for each L and depending upon the pH range of titration, one or more Ls will be important relative to reaction with H^+. Therefore the pH range of titration is significant relative to the final value. Furthermore we can imagine different kinds of alkalinity reflecting the ligand such as carbonate alkalinity, phosphate alkalinity, and total alkalinity relative to the pH titration curve.

It is possible to derive the pH_e of the equivalence point. For a one site reaction (H^+,L, HL), the solution is (Stumm and Morgan, 1970, Aquatic Chemistry, table 3-6):

$$[H]^3 + [H]^2 K - [H](C K + K_w) - K K_w = 0$$

where [ ] are molar concentrations, $K = \frac{[H][L]}{[HL]}$, $C = [HL] + [L]$, and $K_w = [H][OH]$, and the equivalence point is defined by: $[H] = [L] + [OH]$. (NB: in the above discussion the reaction of H^+ with OH^- was not included, but in any aquatic titration, OH^- will be present. Also in the above and following equations, + and - have been deleted for simplicity; Thus $[H^+] = [H]$).

For a diprotic reaction, involving H_2L, HL^-, L^{-2}, H^+ and OH^-, the solution for the equivalence point is:

$$[H]^4 + [H]^3 K_1 + [H]^2 (C K_1 + K_1 K_2 + K_W)$$
$$- [H] K_1 (C K_2 + K_W) - K_1 K_2 K_W = 0 \qquad (1)$$

where

$$K_2 = \frac{[H][L]}{[HL]} , \quad K_1 = \frac{[H][HL]}{[H_2L]} , \quad C = [H_2L] + [HL] + [L]$$

and the equivalence point is defined by:

$$[H] = [HL] + 2[L] + [OH]$$

For most natural waters, the system that is modelled for alkalinity is carbonate alkalinity and involves H_2CO_3, HCO_3^-, CO_3^{-2}, H^+ and OH^-. This is a two-proton acid and the solution for alkalinity ($[HCO_3] + 2[CO_3] + [OH] - [H]$) follows the above relationships. Therefore, the equivalence point is when: $[H] = [HCO_3 + 2[CO_3] + [OH]$

and $C = [H_2CO_3] + [HCO_3] + [CO_3]$

and $K_2 = \frac{[H][CO_3]}{[HCO_3]}$, $K_1 = \frac{[H][HCO_3]}{[H_2CO_3]}$

The actual equivalence point pH is defined by equation (1). Note that there are two important points in this definition of carbonate alkalinity. (NB: carbonate alkalinity rather than alkalinity is used to denote that the alkalinity system is based upon the carbonate dissociation model.) First of all, the actual total carbonate must be known in order to be able to define the end-point (C in equation (1)). Secondly, the system is assumed to be defined by carbonate dissociation only. (We have taken care of this point by carefully noting carbonate alkalinity and not simply alkalinity.) But there is no way of knowing beforehand what the total carbonate of a system will be. Therefore, in the general sense, one can not assume a specific end-point for alkalinity titration in a natural system.

It is worthwhile to see where the endpoint of pH = 4.5, mentioned in "standard methods" comes from. A simple solution

of the fourth order equation (1) for all values where C is greater than 10^{-6} M and for carbonate dissociation values of K_1 and K_2 is:

$$[H] = (C\ K_1 + K_W)^{0.5} \qquad (2)$$

When $CaCO_3$ is saturated with respect to water and in equilibrium with atmospheric CO_2, C $\sim$ 0.002 M. Substituting this value in equation (2) along with $K_1 = 10^{-6.4}$ and $K_W = 10^{-14}$, gives a pH of 4.55. However, if the C is 10^{-5} M, more typical of a soft-water environment, the result for the end-point from equation (2) is a pH of 5.7, etc. Therefore, it is incorrect to use a fixed end-point titration of 4.5 for all kinds of water because a) the alkalinity may not be due to carbonate species, and b) the total carbonate concentration varies. A most important conclusion is that as the alkalinity decreases, the error due to titration to a fixed end-point increases.

There is a way in which this can be overcome. One may approach the problem through a proton balance rather than an equivalence point. For a titration, we may write:

$$H^+\text{-reacted} = H^+\text{-initial} + H^+\text{-added} - H^+\text{-remaining}$$

Translating this into system variables:

$$\text{alkalinity} = \frac{[H]_i\ V_s + V_a\ C_a - (V_a + V_s)[H]_f}{V_s} \qquad (2a)$$

where $[H]_i$ = initial solution H^+-ion concentration (eq/L) measured by pH

$[H]_f$ = final solution H^+-ion concentration after acid addition measured by pH

V_s = vol sample (ml)

V_a = volume acid added (ml)

C_a = concentration acid (eq/L)

and units of alkalinity are eq/L.

The problem with this approach is that one is assuming that the pH scale is an H^+-ion concentration scale. This is not true in general, and even given an initial proper calibration, if the titration is not carried out at constant ionic strength, due to addition of acid, the final H^+-ion concentration calibration will not be equal to the initial calibration. Therefore, for accurate results, a constant ionic strength medium is required, and the pH electrode should be calibrated in this medium against a known acid. Then assuming the salt added for constant ionic strength adds negligible H^+ or OH^-, the mass balance equation is valid. Details and procedures of this method are discussed later on.

Note that this method does not precisely give alkalinity as defined earlier. The proton balance method results in:

$$[H^+\text{-reacted}] = 2[CO_3^=] + [HCO_3^-] + [OH^-]$$

for a simple carbonate system, whereas the definition of alkalinity for the same system is:

$$\text{Carb. alk.} = 2[CO_3^=] + [HCO_3^-] + [OH^-] - [H^+]$$

Another and more precise method of approach relies on the Gran titration. Gran (1952) calculated functions for titration curves that result in linear functions for portions of the titration curves. In alkalinity determinations, then, portions of the titration curve are made linear, and a linear least squares analysis of a series of titration data results in a determination of the equivalence concentration.

Imagine the carbonate system. Then at any point on the titration curve:

$$\text{Carb. alk.} = [HCO_3^-] + 2[CO_3] + [OH] - [H] \qquad (3)$$

and the equivalence point is: $[H] = [HCO_3] + 2[CO_3] + [OH]$

and the equivalence point for the reaction: $CO_3^= + H^+ = HCO_3^-$ results in an expression valid for any point on the titration curve:

$$CO_3\text{-alk} = [CO_3] + [OH] - [H] - [H_2C] \quad (4)$$

and the equivalence point is: $[H] = [CO_3] + [OH] - [H_2C]$

Note that both carb.-alk. and CO_3-alk. are conservative terms that do not vary with pH, etc. Assume the volume of acid to reach the equivalence point for carb.-alk. is V_2 and for CO_3-alk. is V_1; the acid concentration is C_a, and sample volume is V_s. Then:

$$V_2\ C_a = V_s \text{ (carb.-alk.)} \quad (5)$$

and $$V_1\ C_a = V_s \text{ } (CO_3\text{-alk.}) \quad (6)$$

and note that total carbonate, C = eq.(3) - eq.(4); or, substituting in eq.(5) and (6):

$$(V_2 - V_1)\ C_a = V_s\ C \quad (6a)$$

Since alkalinity and carbonate alkalinity are conservative over the entire titration curve, then at any point on the titration curve the relationships relative to these two parameters and their equivalence points must hold for both positive and negative values. Hence for V-volume of acid added:

$$(V_2 - V)\ C_a = (V_s + V) \text{ (carb.-alk.)} \quad (7)$$

and $$(V_1 - V)\ C_a = (V_s + V) \text{ } (CO_3\text{-alk.}) \quad (8)$$

Another way of looking at (7) and (8) is that the right sides of the equations are the number of equivalents in a given sample; the only factor that can change these conservative parameters is the volume. The left sides of the equations are the number of equivalents (of acid) to be reacted with the parameter relative to the equivalence point. The procedure for linearization is as follows:

1) Use regions of definition of carb.-alk. and CO_3-alk. where one parameter predominates. Therefore, when excess acid beyond the equivalence point for carb.-alk. is added ($V > V_2$), equation (3) becomes:

$$\text{(carb.-alk.)} \rightarrow [H]$$

and substituting in eq.(7) for $V > V_2$:

$$(V_2 - V)\ C_a = -(V_s + V)[H]$$

or: $$(V - V_2)\ C_a = (V_s + V)[H] \qquad (9)$$

Equation (9) in essence implies there are negligible carbonate ions to react, and the system [H] (pH) is determined merely by the dilution factor $(V_s + V)$.

Defining a function, F_1, by:

$$F_1 = (V_s + V)[H] \qquad (10a)$$

$$= (V_s + V)\ 10^{+\log [H]}$$

a linear function results:

$$F_1 = a + b\ V \qquad (10b)$$

When $F_1 = 0$; $V = V_2$, or

$$V_2 = -\ a/b \qquad (10c)$$

from eq.(9), $b = C_a$. (10d)

Note that this equation is only valid for the assumption made and for H^+-ion concentrations. Hence, only values quite removed from the equivalence point are valid, and the "pH" used must measure concentration. The latter point can only be obtained by working at constant ionic strength obtained by adding a neutral salt or by correcting for activity changes, junction potentials, etc., with each addition of acid.

V_1 can be obtained by simplifying equations (3) and (4) between V_1 and V_2. This is the range where $[HCO_3] > [CO_3]$, [OH], [H] and $[H_2CO_3] > [CO_3]$, [OH], [H], or eq. (3) and (4) become for $V_1 < V < V_2$:

$$(\text{carb.-alk.}) \rightarrow [HCO_3] \qquad (11)$$

and $$(CO_3\text{-alk.}) \rightarrow -[H_2CO_3] \qquad (12)$$

substituting (11) in (7), and (12) in (8), we get:

$$(V_2 - V)\ C_a = [HCO_3] \tag{11a}$$

and $$(V - V_1)\ C_a = [H_2CO_3] \tag{11b}$$

But, from $K_1 = \frac{[H][HCO_3]}{[H_2CO_3]}$, $[H_2CO_3] = \frac{[H][HCO_3]}{K_1}$

we can substitute in (11b) for H_2CO_3 and get :

$$(V - V_1)\ C_a \frac{K_1}{[H]} = (V - V_1)\ K_1 \tag{12}$$

Defining F_2 as the left-hand side of (12)

$$F_2 = (V_2 - V)\ [H] = (V_2 - V)\ 10^{\log[H]} = (V - V_1)\ K_1 \tag{13a}$$

we obtain for the assumptions made ($V_1 > V > V_2$), a linear function:

$$F_2 = a' + b'\ V$$

and when $F_2 = 0$, $V = V_1$, or

$$V_1 = - a'/b' \tag{13b}$$

and from equation (13), the slope is K_1, or

$$K_1 = b' \tag{13c}$$

Having determined V_1 and V_2, we may obtain C, the total carbonate, using equation (6a). Once again one must remember the limiting assumptions and the need to measure H^+-ion concentrations.

Methods of Analysis

a. Short method:

This method is based upon the titration and determination of alkalinity using the proton balance procedure (eq. 2a) in a constant ionic strength medium. The pH electrode is calibrated with a known concentration of acid in a fixed ionic strength medium so that pH (or mV) readings can be correlated to H^+-ion concentration values (see next section).

Constant ionic strength medium: A 0.01 N NaCl or KCl medium has been used. A 50 - 100 ml or 50 - 100 g sample is measured out into a 250 ml beaker or Erlenmeyer flask. The sample may be filtered or not depending upon the end use and interpretation of the results. A top-loading balance of 1 kg capacity and 0.01 g sensitivity is excellent for measurement. Alternately volumetric ware may be used. Add 1 ml of N NaCl to the sample and mix. Insert stirring bar and pH electrode.

Titrate to 3 variable end-points, using standardized HCl. Typical end-points might be pH - 4.2, 4.0, 3.8. For alkalinities of about 0.001 eq/ℓ, use 0.1 N HCl for 0.0001 - 0.00001 eq/ℓ alkalinity, use 0.01 N HCl. These values of alkalinity and acid will consume between 0 - 2 ml of HCl. Use a micro-burette for titration. Small volumes of acid are required to maintain constant ionic strength.

pH calibration: Titrate a blank solution consisting of 1 ml of 1 N NaCl in 100 ml of freshly prepared double distilled water with 0.1 N HCl. Measure the pH using a gel combination electrode while stirring the solution. The H^+ ion concentration for this solution is:

$$(V_s + V_a)[H] = C_A V_A$$

or:
$$[H^+] = \frac{C_A V_A}{V_s + V_a}$$

Make a plot of $-\log [H^+]$ vs. pH or mV readings; or calculate a linear least squares fit to the data. A linear function should result, with a slope of 1 for pH calibration and a slope of 0.059 mV/log unit, when the electrode is functioning properly, for calibration at 25°C.

A reference"standard" of 10^{-4} M HCl in 0.01 NaCl may be used to check the electrode during analyses. Use this "pH" - log [H] relationship to determine [H].

The alkalinity may be calculated from either eq.(2a) for the three different end-points with an average determined, or calculations using the Gran analysis; eq. (10a),(10b) and (10c); can be carried out. If a programmable calculator is handy, more pH data points (5 - 6) can be obtained using the Gran procedure. Furthermore, for low alkalinities ($<10^{-5}$ eq/ℓ), organic acids may contribute to the alkalinity. If this is the case, titration to lower pH's ($-\log [H^+] = 3.3$) may be desired.

If the alkalinity is determined by a proton balance, eq. (2a), carbonate alkalinity is:

$$A_C = 2[CO_3^{=}] + [HCO_3^{-}] + [OH]$$

whereas if the alkalinity is determined by a Gran analysis, carbonate alkalinity is:

$$A_C' = 2[CO_3^{=}] + [HCO_3^{-}] + [OH^{-}] - [H^{+}]$$

The two are equivalent when the $[H^+]$ at the equivalent point is added to A_C'. Hence for C = 0.002 M/L the end-point is about 4.5; and $[H^+] = 0.032$ meq/ℓ. An estimate of the equivalence point H^+-ion concentration can be obtained from eq.(2) if a carbonate system is assumed. As estimate of C is obtained from the alkalinity and the initial pH from:

$$C = \frac{\text{carb.-alk.}}{(\alpha_1 + 2\alpha_2) + [OH] - [H]} \qquad (14)$$

where $\alpha_1 = \left(\frac{[H]}{K_1} + 1 + \frac{K_2}{[H]}\right)^{-1}$

and $\alpha_2 = \left(\frac{[H]^2}{K_1 K_2} + \frac{[H^+]}{K_2} + 1\right)^{-1}$

Depending upon the initial pH, some of the terms in the denominator of eq.(14) will be negligible.

An estimate of reproducibility can be obtained from repetitive analyses or comparison of results of data points. Using a pH meter readable to $\pm$ 0.01 units, the maximum difference

between points is <1%, and the standard deviation ,

$$S.D. = \sqrt{\frac{\Sigma (X_{meas} - \bar{X})^2}{n - 1}}$$

is typically 1%.

b. Gran analysis for alkalinity.

This method is the preferred method as precise calibration of the pH electrode is not required. Key factors in the analysis are a) electrode linear response, b) accurate volume measurements of sample and acid, and c) accurate calibration of acid.

Check the linear response in the following manner. Measure approximately 50 ml or 50 g of distilled deionized water. Add NaCl or KCl to obtain a constant ionic strength. Using a pH meter, record volume of acid (about 0.01 N) vs. pH or E reading. Using linear least squares statistics, check for linearity in approximate pH range 3 - 7 of

pH or E vs. $\log \frac{V}{V_s}$, where V = volume acid, and V_s = volume sample.

Example for linearity check:

To 50 ml of deionized distilled water, 0.5 ml of 0.1 N NaCl were added, to give 0.001 N NaCl using a toploading balance readable to 0.01 g. 0.012444 N HCl was titrated using a 0-2 ml microburette readable to .001 ml. The following data were obtained when a portable digital pH meter readable to 0.01 units was used with a gel reference combination electrode in a stirred solution:

(1) vol. acid (ml)	0	.1	.2	.3	.4
(2) total volume	50.5	50.6	50.7	50.8	50.9
apparent pH	5.27	4.48	4.15	3.96	3.98
-log (1)/(2)	-	2.704	2.404	2.229	2.105

R = .9999 for least square fit.

This test equation is derived from:

$$[H] = \frac{V_a C_a}{V_a + V_S}; \text{ and } pH' = C + d \log \gamma_H [H]$$

or: $$pH' = C + d \log \gamma_H \frac{V_a C_a}{V_a + V_S}$$

$$pH' = [C + d \log \gamma_H C_a] + d \log \frac{V_a}{V_a + V_S} \qquad (15)$$

where pH; = apparent pH (or E); γ_H = activity coefficient of H^+-ion; C_a = concentration of acid; and V_a and V_S are acid volume and sample volume, respectively.

If the pH electrode response is linear, the precise [H] - pH value need not be known. This can be seen as follows:

assume: $pH' = C + d \log [H]$

substituting for [H] in equation (10a):

$$(V_2 - V)\ 10^{(pH'-c)/d} = F_1$$

where C and d are constants defined by the experimental conditions; d should be nearly 1, whereas C depends upon the calibration setting.

The acid volume may be obtained from the slope of the linear least squares fit for F_1 (eq. 10b). But due to variations in sensitivity it is better to carry out a Gran analysis on a known alkalinity sample of a concentrated acid and to make quantitative dilutions for titrations of unknown samples. To obtain an approximate 0.01 N acid for soft water alkalinity determinations, proceed as follows:

1) weigh out about 50 g of 0.001 N Na_2CO_3 solution. Add 5 ml of 1 N KCl or NaCl to give an approximate 0.1 ionic strength solution;

2) use approximately 0.1 N HCl and obtain titration data to pH' of approximately 3.5;

3) obtain a least squares analysis following equations (10a) and (10b), and pH < 4.0. Obtain V_2 from equation (10c), and

acid concentration, Ca, from equation (5). The acid may be quantitatively diluted to approximately 0.01 N for soft water analyses.

The Gran procedure for soft water is to take about 50 g of sample, add 5 g of 0.1 Na Cl to result in an approximate 0.01 N ionic strength solution (valid for specific conductance measurements <100 μmho/cm) and pH' (apparent pH) or E (EMF) values are recorded over the titration range. Typically a stable pH is read for each 0.1 - 0.2 ml addition of acid.

Suggested equipment suitable for "field determinations" consists of a magnetic stirrer, a 100 - 250 ml beaker or Erlenmeyer flask, a Gilmont 0 - 2.000 ml microburette, a "Digi-sense"® ± 0.01 portable pH meter with combination electrode. Details of analysis are as follows:

a) weigh out 50 ± g of sample in beaker with stir bar. Add by weight NaCl.

b) insert electrodes adjusted to read approximate pH using buffers, and read apparent pH. (Electrode linearity should be checked, and electrodes washed and kept wet in a sample similar to ones being analysed. Care should be taken to wash and blot obvious drops off electrode shield.) Compare field pH value to constant ionic strength value. They should not differ by more than ± 0.3 pH units and typically should agree to < ± .03 units.

c) ready microburette by cleansing in small volume of acid. Load electrode from beaker insuring no bubbles are trapped. (Electrode is best stored "overnight" in wet condition. Dispense about 0.1 ml of acid stopping at a whole number, wipe side of burette with tissue, and place so the tip is just in solution. One ring stand works well for burette and electrodes.) Add increments of acid to an apparent pH of 3.5 - 3.8 and record apparent pH or EMF values. Then follow with either d) or e).

d) visually pick a pH data set of about 4.2 - 4.3 (for soft waters) and carry out an analysis using equation (10a),etc. Delete highest pH data set and repeat. Compare values obtained from goodness of fit to decide whether to retain highest

data set. Determine and record alkalinity using equation (5) and record correlation coefficient and/or standard estimate of error.

e) this procedure can be programmed on a calculator. Starting with the lowest pH data set, carry out a least squares analysis on three points and continue to add another data set until R decreases and/or the standard error of estimate increases. The change will be due to the assumption that $[H] >> [HCO_3]$ is no longer valid.

Two examples follow. Calculations were carried out on a programmed HP-25, using method d).

Example 1:

A lake sample of field pH 6.59, and specific conductivity 25 μmho/cm was titrated with 0.012444 N H Cl as follows: 5.58 g of sample were weighed out and 0.5 g of 0.1 N NaCl added. Data obtained are:

V_a	0	.1	.2	.3	.4	.5	.6	.7	.9	1.1	1.3	1.4
V	55.3	55.4	.5	.6	.7	.8	.9	56	56.2	.4	.6	56.8
pH	6.61	6.30	5.9	5.34	4.76	4.43	4.24	4.11	3.93	3.8	3.75	3.71

Using data sets of V_a = 0.5 ml and greater, least squares analyses using equation (10a) etc., give a =-0.002698, b = 0.10041, R = .99, V_2 = .269 ml and alkalinity = 6.10×10^{-5} eq/ℓ. This results in a standard error estimate:

$$\text{standard error} = \left(\frac{\Sigma\, d^2}{n-1}\right)^{0.5}$$

$$\text{where } d = \frac{F_1(\text{calc}) - F_1(\text{eqn})}{F_1}$$

and n = no. of samples of 6.3%, which is rather poor. Regression eliminating the V_a = 0.5 ml data set does not improve results.

Example 2:

A sample with field pH of 6.06 and specific conductance = 29 μmho/cm is titrated with 0.012444 eq/ℓ acid as follows: weight of sample = 52.57, and 0.5 g of 0.1 N NaCl are added:

V_a	0	.1	.2	.3	.5	.7	.9	1.1	1.2
V	53.07	53.17	53.27	53.37	53.57	53.77	53.97	54.17	54.27
pH'	6.03	5.84	5.57	5.16	4.39	4.08	3.91	3.79	3.74

Regression of data sets of V_a = .7 or greater gives a = -.003083, b = .010796, R = .99999, and V_2 = 0.286 ml. SEE= 0.089%, resulting in an alkalinity of 6.79×10^{-5} eq/ℓ.

Example 2 is in the same watershed and downstream from example 1. Using a carbonate model assumption (equation (3)), $[HCO_3] + 2[CO_3] + [OH] \sim [HCO_3] = 6.12 \times 10^{-5}$ and 6.88×10^{-5} eq/ℓ for examples 1 and 2 respectively.

c. Gran analysis of titration curve.

More information may be obtained by analysis of the entire titration curve. Prepare the sample as in a) in a 0.01 N NaCl medium, calibrate the electrode as before, and obtain approximately 50 data points equally spaced down to a pH of about 3.8 (or lower if organic acids are considered). However, the titration must be carried out in a condensed system isolated from the atmosphere preferably at constant temperature. A jacketed vessel with a glass taper connector for a micrometer burette, a 5 cc syringe for expansion, and a cylindrical pH holder using an "O" ring fit can be constructed quite readily.

The procedure of analysis of the resulting data are based upon obtaining the best fit to a carbonate model, and then looking at deviations in the fit proposing additional monoprotic ligands to improve the fit and obtaining concentrations and dissociation constants.

The procedure for the carbonate curve reduction is as follows:

1) using the last 4 - 5 data points of the lowest pH data sets, obtain a first estimate of V_2 from equations (10a - 10c).

2) using data sets $V < V_2$, obtain an estimate of V_1, using equations (13a) and (13b).

3) obtain an estimate of C from equation (6a) using values of V_1 and V_2 from 1) and 2) above.

4) from $[H_2CO_3] = C\alpha_o$, $[HCO_3] = C\alpha_1$, and $[CO_3] = C\alpha_2$

where: $\alpha_o = (1 + \frac{K_1}{[H]} + \frac{K_1K_2}{[H]^2})^{-1}$

$$\alpha_1 = (\frac{[H]}{K_1} + 1 + \frac{K_2}{[H]})^{-1}$$

$$\alpha_2 = (\frac{[H]}{K_1K_2} + \frac{[H]}{K_2} + 1)^{-1}$$

obtain values for $[H_2CO_3]$, $[HCO_3]$ and $[CO_3]$. Adjust F_1, equation (10a) to

$$F_1 = (V_S + V)([H] - [HCO_3])$$

and redetermine V_2.

6) correct equations (11), (11a), (12), (12a) to:

$$(V_2 - V)\ Ca = [HCO_3] + (2[CO_3] + [OH] - [H])$$

and $(V - V_1)\ Ca = [H_2CO_2] + ([H] - [CO_3] - [OH])$

and proceed to determine V_1. Also obtain the slope, K_1, for use in 4.

7) obtain new values of C as in 3)

8) determine the goodness of fit by the root mean square of differences of F_1 for a, b, and V_a (equations (10a)(10b)) and the relationship:

$$F_1 = (V_S + V_a)([H_2CO_3] + 2[CO_3] + [OH] - [H])$$

with $[H_2CO_3]$, $[CO_3]$ determined as in 4).

9) iterate steps 4) to 7) until the goodness of fit (eq. 8) does not improve, or starts to decrease.

10) determine final carbonate alkalinity, V_1, V_2 and total carbonate

11) make a plot of ΔF_1 (F_{eqn} - F_{exptl}) vs. pH for values <pH = V_1. Examine departures for organic acids.

12) a similar procedure can be carried out for F_2 ($V_1 < V_a < V_2$) for weak inorganic and organic acids.

An alkalinity contribution of about 50 µeq/ℓ is required from sources other than carbonate in order to be detected.

Some analyses have been run on dystrophic waters having 50 - 100 µeq/ℓ alkalinity. No detection of contribution of organic acids could be ascertained, although a complexing method with Cu^{+2} suggested about 30 µeq/ℓ for H^+ in these waters for non-carbonate sources.

Reference

Gran, G. (1952) Analyst, 77, 661.

PART 4.

Susceptible areas in Ontario and Quebec

Figure 1 is a summary of surveys carried out over the past two years of stream crossings. This map shows the land susceptible to acidification by contours of the calcite saturation index (CSI). CSI is defined as:

$$CSI = \log_{10} \frac{K_c}{CP}$$

where K_c = the solubility product for calcite and CP is the concentration product of $[Ca^{+2}][CO_3^{-2}]$, where [ ] are molar concentrations. Details of calulation from measurement of alkalinity and pH or specific conductivity and pH are given in earlier reports. Interpretation of the diagram is than waters with a CSI of 3 or less are well buffered and not suscpetible to acidification; water with a value between 3 and 4 are probably suscpetible, and water with a CSI greater than 4 are susceptible to a reduced pH.

Figure 1 shows that all of the streams sampled in Quebec are suscpetible to acidification. In Ontario, the Atikokan-Quetico area in Northwestern Ontario, The Algoma region of North-Central Ontario, and The Georgian Bay-Muskoka region of Eastern Ontario are areas susceptible to water quality change sue to acidification.

Quebec shows consistently a lower buffering capacity than crystalline rock regions of Ontario. This is undoubtedly due to the source of glacial material. Ontario has a major source component from the Hudson Bay area which contains Paleozoic limestones. Derived soils could be calcareous. But most of Quebec derives its glacial material from the Labrador crystalline rocks which would evolve in non-calcareous sediments. The interfingering of the two glacial sources as can be seen from the glacial map of Canada is at approximately 74° W longitude.

Figure 1. CSI of Ontario and portions of Quebec from stream crossing studies. Areas with a CSI greater than 3 or 4 are susceptible to pH depression below 5 from acidification. . = sample site.

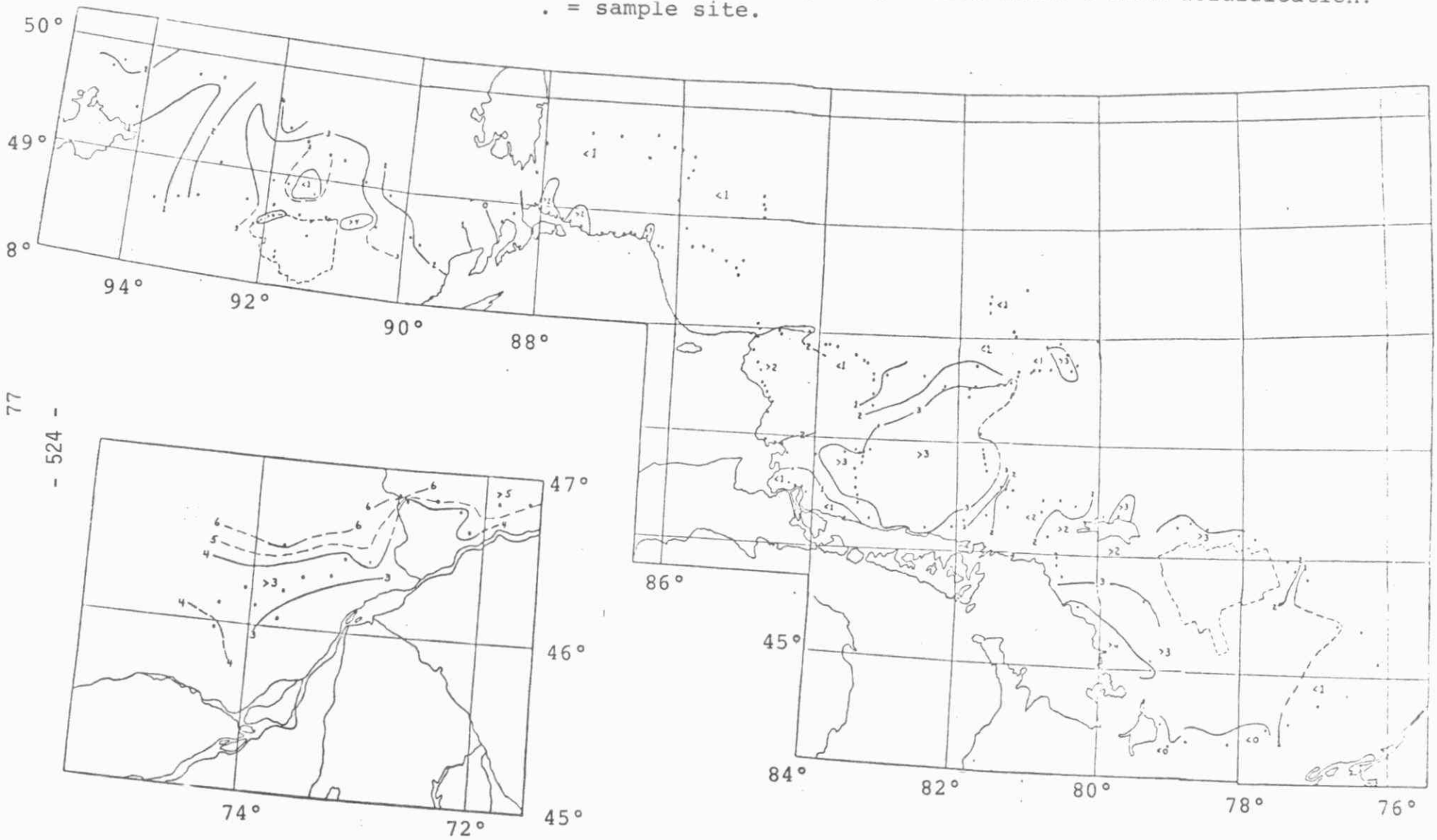
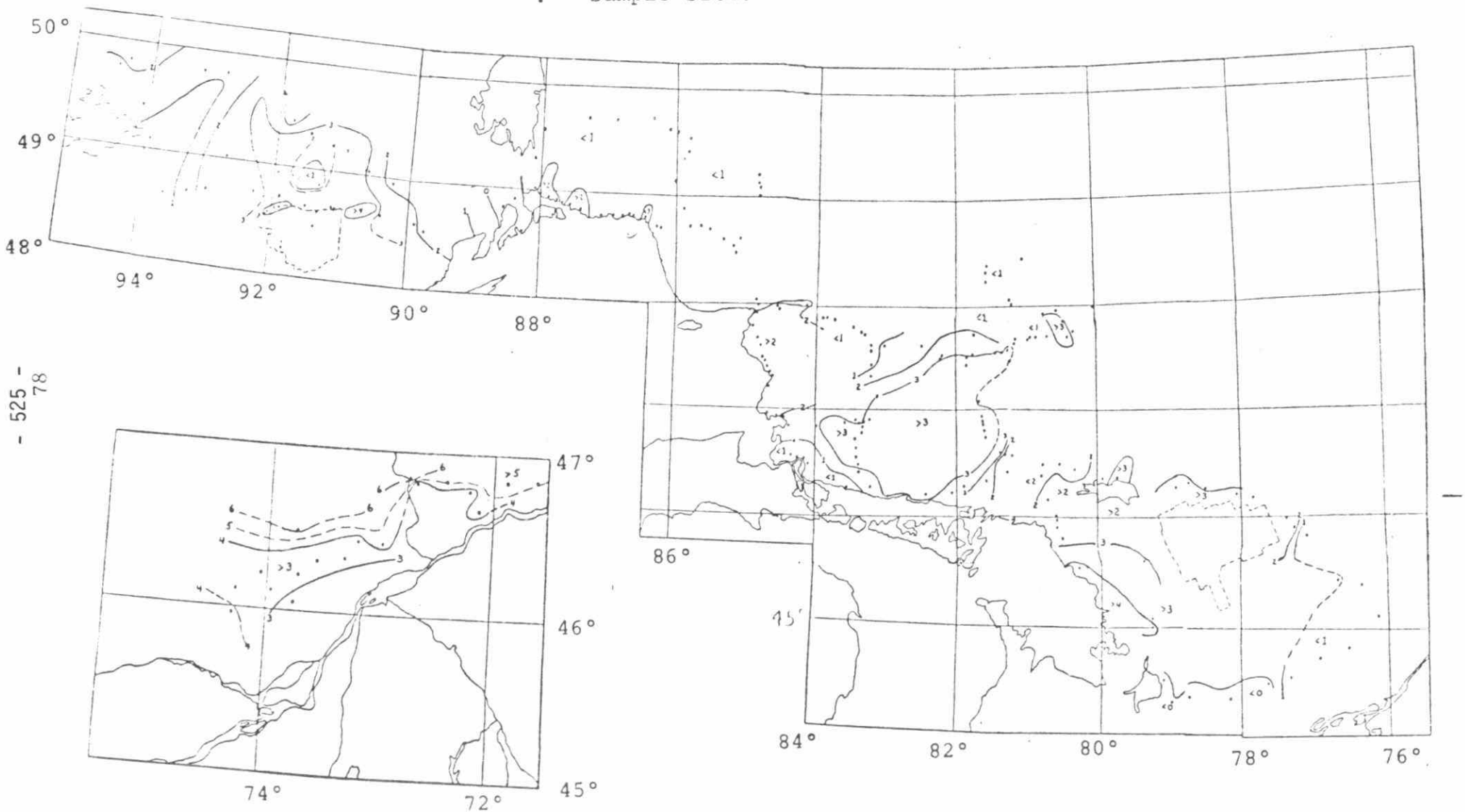


Figure 1. CSI of Ontario and portions of Quebec from stream crossing studies. Areas with a CSI greater than 3 or 4 are suscpetible to pH depression below 5 from acidification. . = sample site.



APPENDIX TWENTY-ONE

ALKALINITY DEFICIENCY AS AN INDEX OF ACIDIFICATION

Mary Thompson

This appendix contains graphs used during M. Thompson's presentation.

INDEX OF FIGURES

28. Explanation of Henriksen's line diagram.

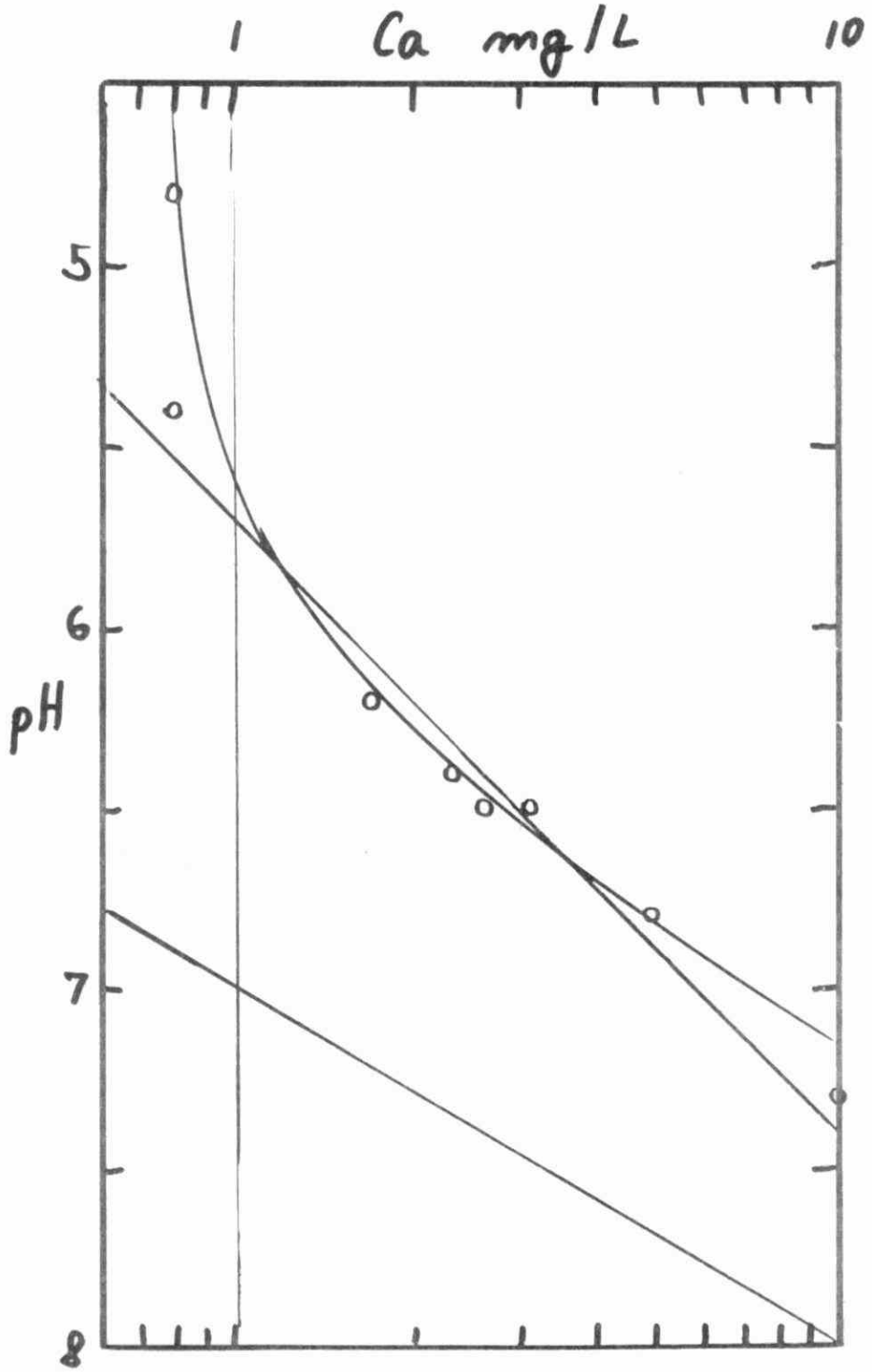
29. Explanation of Henriksen's line equation.

30. Mississagi R. 1957-1958 and 1974.

31. Labrador Lakes.

32. Halifax Lakes.

33. Denudation rate - vulnerability diagram.



28

$$H_2O + CO_2 \rightarrow H^+ + HCO_3^-$$

SET meq Ca^{++} = meq HCO_3^-

ASSUME EQUIL. WITH $P_{CO_2} = 10^{-3.5}$

THEN $pH = 7.0 + 1.0 \log Ca^{++}$

HENRIKSEN'S EMPIRICAL CURVE :

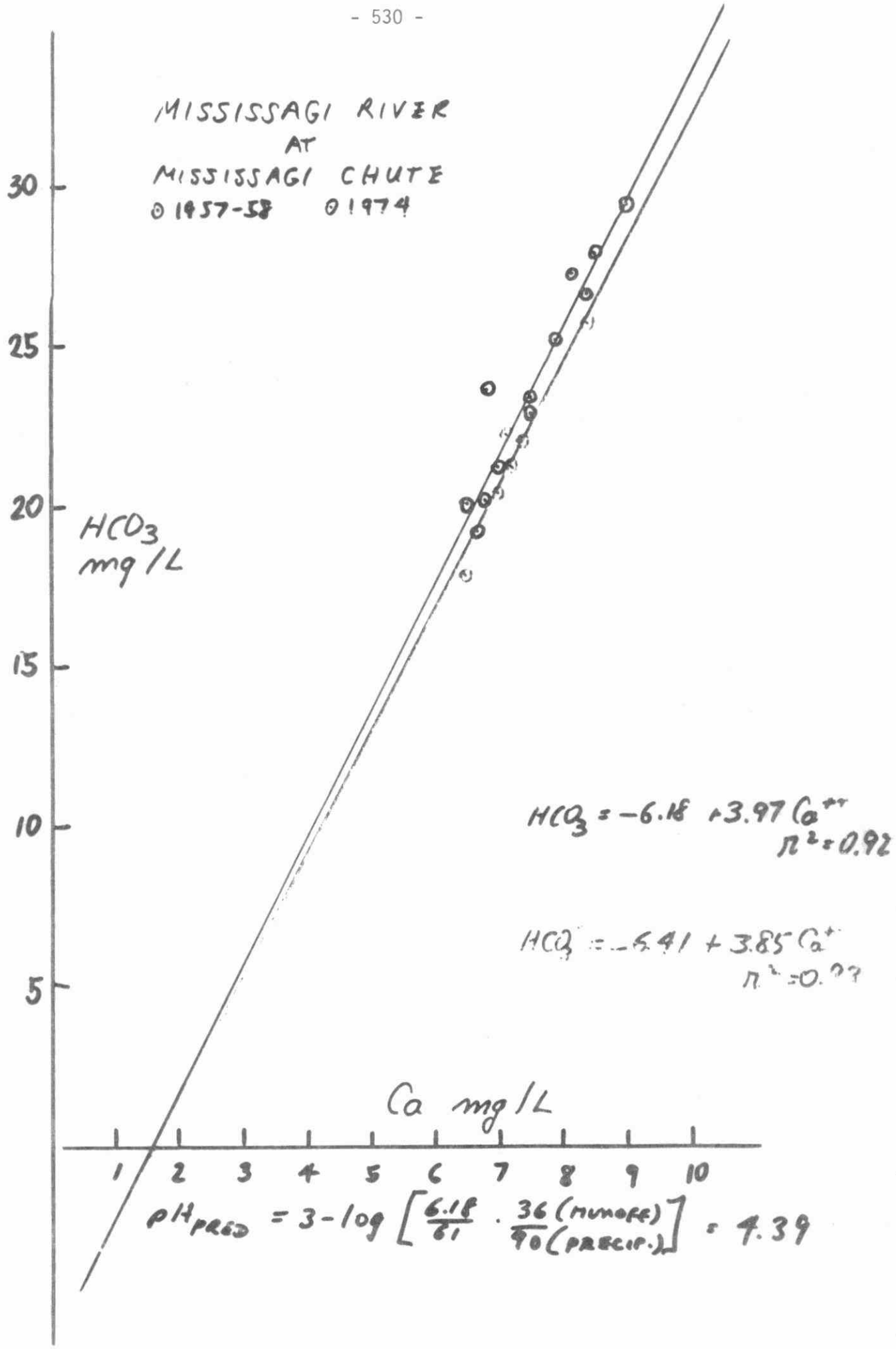
$$pH = 5.7 + 1.7 \log Ca^{++}$$

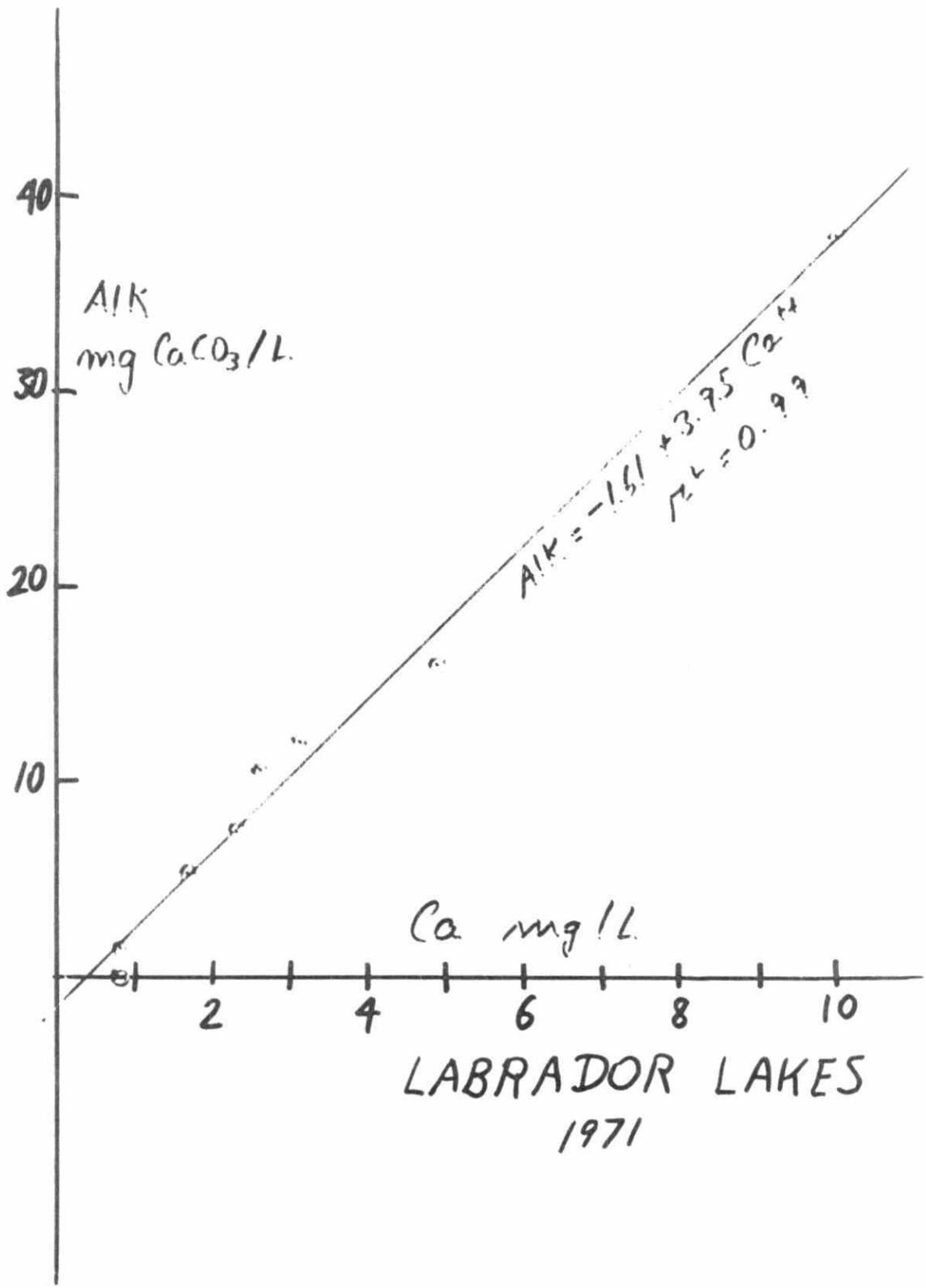
LABRADOR LAKES

$$pH = -3 + \log\left[3.94\, Ca^{++}/50 - 0.055\right] + 7.8 + 2.5$$

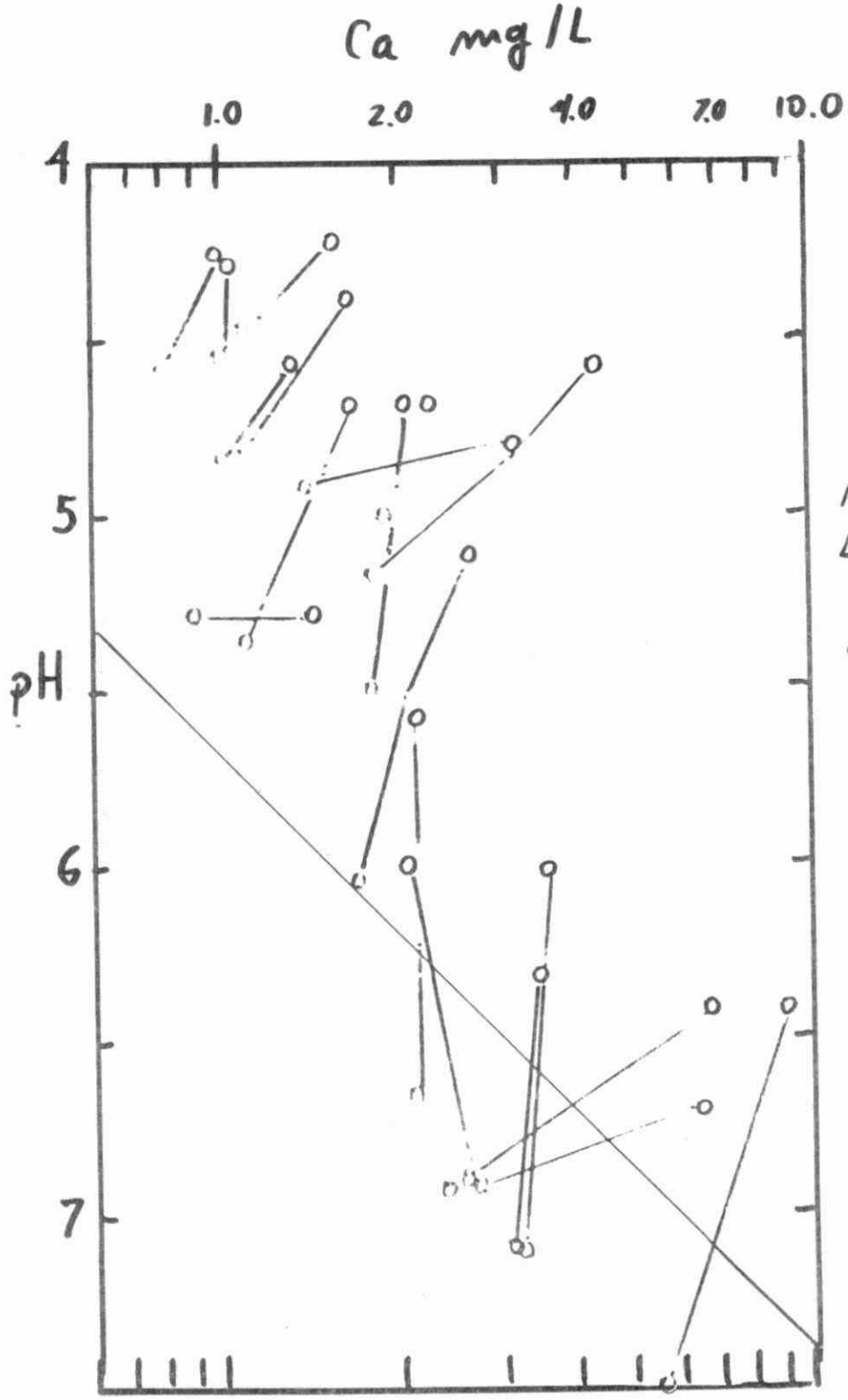
$$Alk\ (mg/L) = -1.61 + 3.94\ Ca^{++}\ (mg/L)$$

$$r^2 = 0.99$$

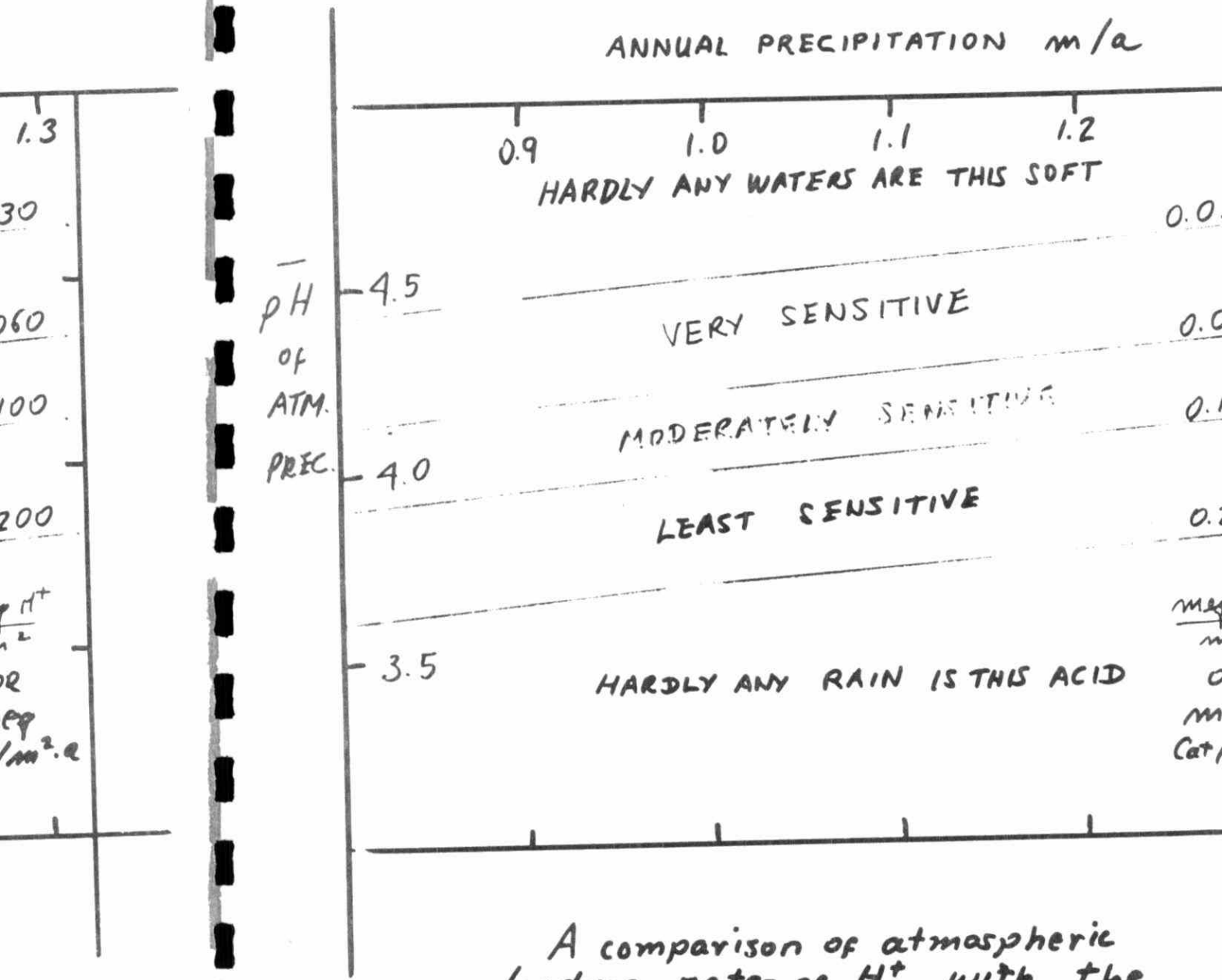

MISSISSAGI RIVER
AT
MISSISSAGI CHUTE
⊙ 1957-58 ⊙ 1974
30
25
20
15
10
5
HCO3
mg/L
HCO3 = -6.18 + 3.97 Ca++
r² = 0.92
HCO3 = -5.41 + 3.85 Ca++
r² = 0.93
Ca mg/L
1 2 3 4 5 6 7 8 9 10
pH pred = 3 - log [6.18/61 . 36 (mmole)/90 (precip.)] = 7.39
30


40
30
20
10
ALK
mg CaCO3/L.
ALK = -1.61 + 3.75 Ca++
r2 = 0.99
Ca mg/L
2
4
6
8
10
LABRADOR LAKES
1971

31


Ca mg/L
1.0
2.0
4.0
7.0
10.0
4
5
6
7
pH
NOVA SCOTIA
LAKES NEAR
HALIFAX
1955 – 1977

32



A comparison of atmospheric loading rates of H^+ with the cation denudation rates of the drainage basins

APPENDIX TWENTY-TWO

THE ECONOMIC IMPLICATIONS OF ACID PRECIPITATION

Introduction

Economics is the study of allocating scarce resources among alternative, often competing, uses. Economists seek to develop objective principles that give guidance in allocating all of the things that are used or are useful to man including his own effort. In addition, these principles help to explain observed economic behaviour and other phenomena as well as to predict the consequences of certain activities.

The cornerstone of these principles is the concept of efficiency. This concept may be defined at different levels of activity. Physical or enginnering efficiency implies that one strives to obtain the most output out of a given level of input. However, economic efficiency focuses on the net value of the output. A firm endeavours to allocate its resources (money, human effort) to maximize the value of its output; its profit. By the same token, all of society's resources should be allocated to uses that will yield the maximum net value of its output. It may, therefore, be possible, at any given time, to reallocate resources - perhaps increasing or even decreasing the amount of money and effort being devoted to environmental management- so that an increase in the net value of society's output will be achieved.

In the context of human welfare, society's resources should be allocated in a manner such that any

. . .continued/

further shifts or reallocations would not make anyone better off.

It is important to realize that these concepts and principles do in fact incorporate environmental quality. Society's output consists of all the things that people value and experience including health, the preservation of other life forms and aesthetic features of the natural environment as well as goods and services that can be bought and sold. Economic theory recognizes that pollution damages and environmental disruptions represent real decreases in the value of society's output and in human welfare. The difficulty,as will be discussed below, is to measure these environmental and social values and incorporate them into empirical assessments and decision-making.

In addition to the efficient allocation of resources, economists are concerned with equity and the distribution of income and economic consequences among individuals, social groups, economic sectors and among nations. Distributive questions about who pays costs, who receives benefits, what people perceive about the equity of a situation all have an important bearing on policy. Unfortunately, economists cannot offer normative guidance about questions of equity or distribution with the potential degree of precision and objectivity that is possible for questions of allocative efficiency.

Nevertheless, economic tools and concepts can be useful to scientists, government officials and the

public as a framework for developing and evaluating relevant information about environmental management problems such as acid precipitation and in making informed decisions about what do do. In addition, insights gained from economic analyses are consistent with an "ecosystem approach". Finally, economic assessments are necessary to develop programs and make choices that strike a balance between environmental protection activities that are timely and effective on the one hand but are not unduly disruptive to the economy on the other.

Problems associated with acidic precipitation are a manifestation of the following, simplified system:

1). Anthropogenic emissions of SO_2 and No_x that are a function of economic activites;

2). Long range international transportation of contaminants;

3). Atmospheric conversion of pollutants to acidic constituents;

4). Deposition of acidic constituents in rain and/or snow;

5). Effects of increased acidity in terrestrial and aquatic ecosystems,some of which are long term and subtle;

6). Economic and social consequencesof the ecological effects and changes.

There are several economic questions that reveal themselves within this system and which must be addressed in the course of resolving acid precipitation problems.

The first fundamental economic question concerns how much money, manpower and effort should be devoted to studying and resolving acid precipitation problems? There are other worthy economic, social and environmental problems that demand attention and resources. On what basis do we determine how much to allocate to acid precipitation rather than some other problem? This is clearly an economic problem and economic principles can be used to base such allocations that can incorporate ecological principles.

Three important information requirements follow this question. First, it is necessary to identify and enumerate the economic and social consequences of the ecological effects and changes wrought by acid precipitation. Second, it is necessary to determine, in a systematic manner, the importance of these effects and consequences relative to other issues and problems. This requires study of the attitudes and preferences of groups and citizens about the ecosystem components damaged by acid precipitation. The third information requirement is the estimation, to whatever detail is possible, of the costs of different methods of resolving the problems as well as the aggregate costs of achieving various levels or degrees or problem resolution.

A second important economic feature of acid precipitation is that damages are borne by jurisdiction different from those who generate the causes. Hence at least part of the costs of control must be borne by entirely

. . .5

different jurisdictions. Quantification of these distributional characteristics is necessary to address a third fundamental economic question; that of the development and implementation of problem resolution programs. These programs will involve several somewhat independent groups or "actors"; the U.S. and Canadian federal governments, the government of Ontario, industrial sources in Canada and the U.S. and affected parties in each of these and other jurisdictions. These "actors" have little direct control over one another so that actions and programs must be developed that contain adequate implementation incentive mechanisms which will effectively induce the relevant parties to undertake the desired control program behaviour. The economic and other incentives facing each relevant "actor" should, therefore, be identified and be made available for negotiations and for policy and program development.

These economic questions and information needs are addressed in more detail in subsequent sections.

Damages from Acid Rain and the Benefits of its Abatement

The principle of allocative efficiency is useful as a criterion to determine how much people, money and effort should be devoted to acid precipitation. This principle is demonstrated in Figure 1. The horizontal axis depicts the level of pollution intensity or environmental quality. The vertical axis represents the total costs of environmental damages and the total costs of environmental protection. Line A on the graph represents

the total costs of environmental protection and cleanup which decline as pollution intensity increases. Line B represents the cost of environmental damages that increase in some direct proportion to pollution intensity. Line C is a summary of both types of costs and indicates that the total costs to society of environmental protection and environmental disruptions are minimized at some point. This level of protection and pollution is considered to be the most socially efficient and can be used as basis for setting objectives.

This analysis implies that some level of pollution damages can be tolerated and that a zero level of pollution is socially as well as economically undesirable. However, this implication rests in the shape and position of the pollution damage function, curve B. New information or knowledge can indicate that the curve should be rotated counter clockwise or shifted substantially to the left. These changes could place the most efficient degree of protection and control at lower levels of pollution intensity. On the other hand, the abatement or control cost function (curve A) may be altered if research and development efforts yield more efficient or cost effective methods of control.

It is substantially easier to develop data and figures for control costs (curve A) than environmental damages. Indeed, the development of abatement cost functions alone are very useful in showing the relevant parties some of the important consequences of the different abatement options or choices

. . .7

available. However, in order to justify and build public support for levels of control that appear to be very costly and which evoke protests from industry,it is imperative that environmental damage cost functions be developed.

The literature on estimating the economic damages of pollution and environmental disruptions is large and growing. Most importantly, there is no general agreement on the methodologies that yield the most accurate or representative measures of environmental damages or their obverse, the benefits of environmental protection and abatement.

These methodologies consist of three basic approaches. The first involves asking people how much they would be willing to pay for various levels of environmental quality and/or protection; the so called "willingness-to-pay" approach. This is accomplished empirically by means of surveys and questionnaires. A second approach assumes that people reveal their preferences for specific levels of environmental quality in their economic activities, especially in the purchase of land and housing. The difference between the value of similar properties in polluted and non-polluted areas is, after suitable adjustments and massaging of the data, attributed to the differences in environmental quality.

A varient of these approaches is the estimation of the value of various recreational resources and activities on the basis of demand functions. The demand functions

reveal individuals' willingness-to-pay for different recreational opportunities that may be destroyed by pollution or restored by pollution abatement. The empirical demand functions are derived statistically from observed behaviour.

A third approach is more direct involving two distinct methodological steps. First, physical damage functions that relate levels of pollution to specific levels of damages or effects on human health, vegetation, property, worker productivity, wildlife, ecosystems, etc. must be developed. These data and relationships in and of themselves provide an important data base on which to make better decisions. The second step is to determine the relative importance of the various physical effects. This is done by assigning the various physical damage units different unit weights such as dollar values. Other weight or ranking systems could be used but using dollar values has the advantage of being directly comparable with the costs of achieving the different levels of control. The important point is that what ever weighting procedure is used in evaluating the benefits of different levels of environmental protection, it should be made explicit.

The approach for developing quantitative information about environmental damages that appears most fruitful with respect to the acid precipitation is this two-step direct method. First of all, the physical damages to all ecological components and human sectors should be enumerated in the appropriate units. The physical relationships among the system components identified in the Introductory Section should be

quantified to the extent possible as well. These damage functions will constitute more or less objective, value-free relationships that indicate the magnitudes, the distribution and, possibly, the functional form of the relevant environmental effects vis-a-vis polluting activities.

The next step is to undertake to determine the relative importance or human significance of the various effects and damages. It is likely that it will be impossible to weight all of the relevant damages in terms of dollar values. Consequently, several weighting or ranking approaches should be undertaken.

For example all of the damages that can be expressed in dollar values can be enumerated and totalled. These results can be used to estimate the relative dollar value of the benefits of different control or abatement programs.

Concurrently with this exercise, surveys can be undertaken to determine the amounts that people are willing to pay for resolution of acid precipitation problems. These results can also be used to express the value of the same postulated mitigation efforts.

Other surveys can be undertaken that attempt to reveal individuals' attitudes and preferences concerning the preservation of terrestrial and aquatic ecosystems that may have been otherwise biased by willingness to pay questions.

As suggested by Victor and others, given sufficient

information, individuals may not be willing to sacrifice certain natural features for other, more conventional economic goods and services, even at substantial personal loss. It may well be that as long as the costs are perceived to be borne equitably, the public will give governments the mandate (or governments may find they have the mandate) to take whatever steps are necessary to resolve the problem. The skillful manipulation of information about damages and public attitudes and the preservation of equity may be the most critical factors in developing and implementing programs. All of these considerations are,of course, consistent with efforts to find the most efficient mix of mitigation programs and level of environmental damages.

In sum, the quantification of the benefits of curtailing acid precipitation will require the following types of information:

1. Ecological and physical damage data
2. Weighting of the relative importance of the physical and ecological damages by means of different methodologies including the assignment of dollar values.
3. Public opinion surveys to determine attitudes and preferences towards the various ecological effects and to provide input for weighting the relative importance of damages.

Additional Sections

The remainder of this paper will include comments on the estimation of the costs of the various approaches for resolving acid precipitation problems. The importance

to policy development of determining the distribution of costs and benefits and the economic incentive structure facing the relevant "actors" will be emphasized. The literature concerning the empirical estimates of the economic effects of acid precipitation will be critically examined and the economic implications for policy development and evaluation will be summarized.

Dr. J. Donnan
Senior Economist
Program Planning &
Evaluation Branch

APPENDIX TWENTY-THREE

An *in situ* experiment using limestone to enhance the hatching success of rainbow trout (*Salmo gairdneri*) eggs in an acid lake

John Gunn
Ministry of Natural Resources
Sudbury, Ontario

Bill Keller
Ministry of the Environment
Sudbury, Ontario

ABSTRACT

Eyed rainbow trout (Salmo gairdneri) eggs were incubated within crushed limestone and noncalcareous gravel substrates in acidic (pH ∿ 5.3) George Lake.

Hatching (egg-sac fry) success of eggs in crushed limestone along a sheltered shoreline (interstitial pH 6.2-7.6) was high (86.9%) approaching hatching success in Fairbank, a near-neutral reference lake (97.9%). Eggs incubated in limestone along a windswept shoreline and subjected to periodic depression of interstitial water pH (minimum recorded 5.6) due to wave action, exhibited poor hatching success (57.4%) comparable to results (11.2-57.1%) for eggs exposed within substrates of mixed, noncalcareous gravel ($\bar{x}$ pH 5.2-5.4).

Fry survival (sac fry-swim up stage) was high in sheltered limestone substrates (70.9%), low in wind exposed limestone substrates (23.2%) and very poor (0.2-0.4%) in noncalcareous gravel, further reflecting the differing pH regimes.

Exposure of emergent alevins hatched within limestone to ambient, acidic lakewater resulted in 65.2-78.8% mortality during a five day holding period. Mortality decreased greatly among alevins held at pH 5.6-5.9 (48.0%) and pH 6.1-6.3 (2.0%) at successive downstream locations on the Chikanishing River, which drains George Lake. The small number of alevins which successfully emerged under the acidic conditions within mixed gravel substrates suffered no mortality during five days exposure in George Lake.

The observed biological responses appear directly controlled by pH, however some measure of synergism with trace metals may be implicated.

INTRODUCTION

Depressed pH, due to acid precipitation, is destroying fish stocks in soft water lakes in many areas of the world (Jensen and Snekvik, 1972; Beamish, 1974; Schofield, 1975). Reproductive impairment is generally considered to be the main destructive mechanism (Schofield, 1976), with low pH affecting gonad maturation (Beamish, et al, 1975; Ruby et al, 1978), egg size and number (Mount, 1973; Ozburn, 1976; Craig and Baksi, 1977; Kennedy, 1979), embryo development and viability (Johansson et al, 1973; Mount, 1973; Menendez, 1976; Kennedy, 1979) and fry survival (Ozburn, 1976). The potential coincidence of fry emergence with snowmelt acid pulses for some species (Jeffries et al, 1976), the synergistic effect of low pH and metal toxicity (Hodson et al, 1978; Chakoumakos et al, 1979) and the high sensitivity of many game fish species (Beamish et al, 1975) combine to cast gloom on the future of sports angling in many lakes.

The pH and buffering capacity of lakes and streams can be increased through the addition of neutralizing agents such as limestone or lime (Grahn and Hultberg, 1975). To date, most neutralization experiments have dealt with the treatment of acid mine drainage (Harrison, 1969), unproductive dystrophic lakes (Hasler et al, 1951; Waters, 1956; Waters and Ball, 1957) and aquaculture ponds (Neess, 1949; Bowling and Busbee, 1964; Arce and Boyd, 1975). Some experimental neutralization has been carried out on oligotrophic, acidic (due to acid precipitation) lakes (Hultberg and Grahn, 1975, Scheider et al, 1975; Yan et al, 1977) however, large-scale chemical treatments have been implemented only recently, notably in

Sweden.

Whole lake chemical treatments are expensive and labour intensive, particularly in remote areas. One alternative we have considered, is to restrict treatment spatially and temporally, seeking to protect incubating fish eggs (considered a very sensitive stage), in the hope that resulting fry will survive after leaving the incubation area.

Preliminary investigation into the feasibility of this approach was undertaken by the Ministry of Natural Resources (M.N.R.) Sudbury District and Ministry of the Environment (M.O.E.) Northeastern Region, during the spring of 1979. This report describes the results of an experiment in which rainbow trout eggs were planted within boxes of crushed limestone and noncalcareous gravel in an acid lake. Hatching success and subsequent alevin survival were determined.

THE STUDY AREA

George Lake (46° 08' N, 81° 24' W) was selected as the experimental site since it is easily accessible, exhibits depressed pH attributable to acidic atmospheric inputs, and has a well documented history of pH related fishery problems (Beamish et al, 1975). Fairbank (46° 28' N, 81° 26' W), a near-neutral lake with a healthy natural fish community (M.N.R., 1979) was utilized for reference purposes. The locations of George and Fairbank lakes are shown in Figure 1 and a comparative summary of water chemistry is provided in Table 1.

Both lakes are soft-water, oligotrophic Precambrian Shield waters, however, they differ markedly in chemical composition (Table 1). George Lake is very dilute (conductivity ∿ 37 umhos/cm), poorly buffered (fixed endpoint (T.F.E.) alkalinity ∿ 5 mg/L) and acidic (pH ∿ 5.3). Fairbank Lake has substantially higher ionic strength (conductivity ∿ 65 umhos/cm), (T.F.E. alkalinity (∿ 14 mg/L) and correspondingly higher pH (∿ 7.1). Concentrations of trace metals including nickel, zinc, aluminum, manganese and iron show significant elevations in George Lake in comparison to levels in Fairbank Lake, likely due largely to increased metal dissolution and mobilization under low pH conditions.

MATERIALS AND METHODS

Trout Eggs

Rainbow trout (Salmo gairdneri) eggs were obtained from two sources: Normandale Provincial Hatchery and the Sault Ste. Marie Research Station (M.N.R.). The Normandale eggs were from brood stock maintained at the hatchery (>50 years), while the Sault Ste. Marie eggs were stripped from wild Lake Superior fish (details provided in Table 2).

The eggs were obtained 3-4 weeks after fertilization in eyed-up, hard condition (dead eggs previously removed). Eggs were measured out in 30 ml aliquots and loaded into the incubation chambers of Whitlock Vibert Boxes (WVB). (WVB are molded clear plastic containers (145 x 90 x 60 mm) used to plant trout eggs in stream beds. They have two compartments: an upper incubation chamber and a lower, larger nursery chamber. The boxes are perforated, permitting good water circulation but preventing the entry of predators). Sample aliquots were set aside for subsequent egg counts. The loaded WVB were wrapped in wet cloth and packed in ice-filled coolers for transport, by truck, to the study lakes (5-12 hr. duration).

Hatching Box Construction and Installation

Hatching boxes (60 x 60 x 30 cm) were constructed of galvanized metal screen (0.6 cm) framed with plywood (1.8 cm) and spruce studding (Figure 2). The sides of the boxes were further covered with fiberglass window screen (7 bars/cm).

A shelf (15 x 60 x 10 cm) was built into each box to keep the WVB level (to avoid crushing eggs) and above bottom (away from silt). The WVB protected eggs and fry from burrowing predators (e.g.: crayfish, sculpins) and confined the eggs for easy hatching rate determination. Previously washed substrate (experimental ∿ 5 cm diameter limestone; control ∿ 5 cm diameter mixed noncalcareous gravel) was placed in the hatching boxes at lakeside. Three WVB, filled with eggs, were carefully buried (to a depth of ∿ 10 cm) in each hatching box and the boxes were positioned in the respective lakes.

The experimental site was located at the outlet of George Lake in Killarney Provincial Park. Twenty hatching boxes were set up 3-10 m upstream of the riffle marking the beginning of the Chikanishing River (Figure 3). Experiments with the Normandale eggs were conducted along the south shore while Lake Superior eggs were used on the north shore. Water depths (0.5-1.5 m) were similar for both sets however the south shore was wind-exposed with a sand substrate while the north shore was sheltered and detritus covered.

All boxes containing limestone were set downstream from boxes filled with mixed gravel to prevent alteration, by limestone, of ambient conditions in the controls.

Half the hatching boxes were left uncovered in shallow water (∿ 0.5 m) for determination of egg-sac fry survival rate. In the shallow uncovered boxes the WVB could be easily uncovered and inspected. The remaining boxes (situated at depths of 1.2-1.5 m) had fry emergent traps (Collins, 1975)

fastened to their tops. A strip of foam rubber was applied between the contact surfaces to maintain a tight seal. Boxes with the attached emergent traps were used to determine egg-alevin survival rate.

Duplicate experimental (limestone) and control (mixed gravel) hatching boxes were equipped with sampling tubes (5 cm diameter plastic pipe) to permit collection of interstitial water. The bottom of each tube (heavily perforated for 15 cm to allow water inflow) was fitted into an empty WVB fastened to the shelf with staples. Because of the presence of the tube, boxes modified for water sampling contained only two WVB holding eggs. Sampling tubes were installed only in shallow set boxes; one in limestone and one in mixed gravel along each shore.

Emerging alevins were captured in, and removed from, the glass bottle (1.8 L) at the apex of each pyramid shaped trap (see Figure 2). At the commencement of hatching, three alevin holding pens (empty hatching boxes with hinged covers) were placed in the lake proper: one for fry from Normandale experimental (limestone) boxes; one for fry from Lake Superior experimental (limestone) boxes; and one for fry from the control (mixed gravel) boxes (stocks combined). Two additional holding pens were later placed in the Chikanishing River at downstream distances of ∿70 m and ∿1000 m.

The reference site was located near the boat dock at Fairbank Lake Provincial Park (Figure 4). The site was windswept, the substrate coarse gravel, and the water depth 0.5-1.0 m.

Three hatching boxes of Normandale eggs and one of Lake Superior eggs were used at this location. Mixed gravel was provided as the substrate in all boxes. One of the boxes holding Normandale eggs contained a water sampling tube. No emergent traps were available for use at the Fairbank site, therefore boxes were covered with window screen during the period of emergence. A holding pen for emerging fry was located approximately 3 m from the hatching boxes.

Sampling

WVB containing Normandale eggs (fertilized April 17 and transported to George and Fairbank lakes on May 10 (day 23)) were left undisturbed until hatching was completed. Eggs were recovered from George Lake on May 25 (day 38) and from Fairbank Lake on May 28 (day 41). After removal of the WVB, dead eggs (white, opaque) and live and dead sac fry were counted and preserved (5% formalin). Egg mortality rate was determined from the ratio of observed dead eggs to the original egg count. The count of live sac fry was not a reliable measure of survival as some fry were able to escape from the WVB and were consumed by predators. Five sac fry were found in the stomach of a sculpin (Cottus cognatus) discovered within the gravel of an uncovered hatching box at Fairbank Lake.

Lake Superior eggs (fertilized on April 23-25 and transported to the study lakes on May 24 (day 29-31)) were recovered and counted on June 7 (day 43-45) from both lakes.

Collection bottles on the emergent traps in George Lake were checked twice a week until the first fry was observed, after which collections and counts were conducted daily. Since emergent traps were not installed at the Fairbank Lake site, alevins were collected by covering the top of the hatching boxes with window screen during the swim up period. The boxes were retrieved into shallow water, the screen removed and the alevins were captured with a dip net.

A five day holding period was used for determination of alevin survival rate in both lakes. The alevins in the holding pens were fed daily with formulated feed ad libitum.

The experiment was terminated on June 28 and all gear, with the exception of a single sampling tube equipped box (NL-1; Figure 3), was removed.

Between May 15 and June 28, water samples for chemical analyses were collected approximately twice weekly from the George Lake site. Samples were obtained weekly from Fairbank Lake between May 16 and June 21.

During each visit, samples were taken from the hatching boxes equipped with sampling tubes and upstream of the experimental installations. Ambient lakewater was collected by hand holding sample bottles below the lake surface. Interstitial water within the hatching boxes was withdrawn from the sampling chamber using a plunger type manually operated bilge pump connected to 1.2 cm diameter tygon tybing. Metal sampling by means of the bilge pump was unsuitable due to contamination by metal parts of the apparatus. In

order to obtain data on trace metal concentrations within the hatching boxes, an electrically operated peristaltic sampling pump (no contact of sample with the pump) was obtained and the single hatching box remaining in situ after termination of the experiment (NL-1), was sampled on two occasions.

Samples for pH, alkalinity, conductivity and major ion analysis were taken in clean 1000 ml glass bottles. An aliquot of each sample was used for measurement of pH (Radiometer model 29 meter) either in the field or within a few hours of collection at the Sudbury field laboratory of M.O.E. Samples for trace metal analyses were collected in acid washed 500 ml polyethylene bottles and were immediately preserved with 1 ml of concentrated nitric acid to retain metals in solution. All bottles were rinsed at least twice with sample prior to final filling. Samples were submitted to the M.O.E. Laboratories, Toronto for analyses.

Additionally, during each sampling event, at each location; temperature and dissolved oxygen measurements (YSI model 54 meter) were performed on interstitial and ambient lakewater.

RESULTS

Water Chemistry

Significant alteration of ambient water chemistry (presented in Table 1) occurred within the limestone filled hatching boxes (sampled at NL-1 and SL-1) incubated in acidic George Lake. Based on mean values (see Table 3) observed effects included pH elevations of ∿ 1 unit and increases in T.F.E. alkalinity (∿100%), conductivity (∿20%) and calcium concentrations (∿55%). Exposure to limestone did not result in any apparent increases in waterborne concentrations of other major ions. Mean pH differred between hatching boxes located along the south and north shores (6.3 and 6.6 at NL-1 and SL-1 respectively) and interesting differences in temporal pH variation, related to wind induced water movements within the outlet area, were noted (Figures 5 and 6).

Monitoring of NL-1 revealed a period of pH depression (May 25-30) associated with high (∿ 50 kph) winds and severe wave action (resulting in rapid displacement of interstitial water with fresh, acidic, lakewater). During this event, interstitial water pH declined to 5.6-5.8, only ∿ 0.3 units higher than ambient lakewater. Subsequent to the acidic pulse, pH increased, and with the exception of a single extremly high value (8.5 - June 12) remained between 6.0 and 6.9 for the duration of the experiment. The anomalously high pH recorded on June 12 may be associated with increasing periphytic growths observed on the box screening (and resultant photosynthetic activity). However, visual examination of the sample collected on that date indicated the

presence of a large quantity of extremely fine suspended particles which apparently resulted from grinding action of the limestone during the previous period of high turbulence. Chemical reaction of these particles (presumably limestone) may account for the highly elevated pH; unfortunately the sample was lost in transit to the laboratory and chemical analyses are not available to verify this hypothesis.

The pH in hatching box SL-1 (maintained between 6.2 and 7.6 throughout the exposure period - see Figure 6) did not exhibit the high degree of fluctuation observed at NL-1, a reflection of its more sheltered aspect. It should be noted that the sampling period of SL-1 (May 30-June 28) was shorter than that of NL-1 (May 15-June 28). Commencement of sampling at SL-1 coincided with the period of pH depression observed at NL-1, however no similar wind induced effect occurred at this more protected location.

Interstitial water within hatching boxes containing mixed gravel (sampled at NG-1 and SG-1) generally maintained slightly higher pH ($\bar{x}$ 5.4-5.6) than ambient George Lake water ($\bar{x}$ - 5.3) likely reflecting periphytic algal photosynthesis and/or very limited buffering by mineral particles associated with the substrate.

No change in ambient water chemistry was found within the hatching box (mixed gravel) sampled in Fairbank Lake (May 15-June 21).

Monitoring of temperature and dissolved oxygen concentrations indicated that similar thermal and oxygen conditions existed in the open lake waters and within the hatching boxes. Between commencement and termination of the experiment, water temperatures increased from 10 - 19°C within boxes incubated on the south shore of George Lake and from 13 - 19°C in boxes located on the north shore. Dissolved oxygen was maintained between 8.9 and 12.0 mg/L (∿100% saturation) in all hatching boxes sampled. Temperature and dissolved oxygen varied from 7.0 - 18.0°C and 9.2 - 12.2 mg/L (∿100% saturation) within the hatching box sampled in Fairbank Lake.

As indicated, only a very small data set (2 samplings at a single location) on trace metal concentrations within the limestone filled hatching boxes was obtained. The available data (Table 4) suggest little alteration of waterborne trace metal concentrations attributable to the influence of limestone. It may be speculated that effects, by limestone, on metal levels (through surface adsorption and decreased solubility resulting from pH elevation) would be greatest during the early stages of exposure (i.e. fresh surfaces available) and data collected after a considerable incubation period may not truly represent the situation. This may be the case, however, inspection revealed no visible metal precipitate on the limestone and reactivity (as reflected by pH) remained generally high throughout the experiment. Additional experimentation would be required to accurately define the extent of limestone trace metal interaction.

Accessory sampling conducted on the Chikanishing River downstream of the experimental installation revealed a dramatic elevation in river pH with increasing distance downstream. Data collected on June 20th, showed an almost linear pH increase from the outlet of George Lake (pH - 5.6) to the mouth of the Chikanishing River (pH - 6.7), a distance of ∿2 km. This phenomenon appears attributable to neutralization by groundwater inputs (numerous inflowing springs were observed) and changing substrate geochemistry (large clay deposits).

Hatching Success and Alevin Survival

No difference in the hatching success (egg-sac fry) of eggs incubated in limestone ($\bar{x}$ 57.4%) versus mixed gravel ($\bar{x}$ 57.1%) was noted for the first set of eggs (Normandale) placed along the south shore of the George Lake outlet (Table 5). The poor hatching success in the limestone filled hatching boxes at this location appears to be a direct result of the previously outlined, wind driven acidic pulse which reduced interstitial water pH to 5.6-5.8; approaching pH in the lake and within the gravel filled boxes (5.4-5.5) during that period (May 25-30). The contrasting high hatching success rate ($\bar{x}$ 93.7%) in Fairbank Lake (on a similar wind swept shoreline) ruled out mechanical damage as responsible for the high mortality in George Lake.

Hatching success in the limestone filled boxes was much improved among the second set of eggs (Lake Superior stock) placed along the sheltered north shore and thus protected from wind induced pH depression. At this location, hatching

success was 86.9% in the limestone filled boxes (pH 6.2-7.6) versus 11.2% in boxes containing mixed gravel (pH 5.4-6.0). In Fairbank Lake the hatching success rate for Lake Superior eggs was 97.9% (only one box used).

Interestingly, hatching success within mixed gravel (George Lake controls) was considerably reduced among the second set of eggs (Lake Superior stock - 11.2%) in comparison to eggs from Normandale, introduced 14 days earlier (57.1%). The differential hatching success observed appears to be a direct result of the synergistic effect of increased water temperature and low pH (Kwain, 1975; Robinson et al, 1976). Mean water temperatures increased ∿3.5°C between the respective hatching rate determinations (Normandale stock, May 10-25, 10-14°C; Lake Superior stock, May 24-June 7, 14-17°C).

The first emergent alevin of Normandale stock (still with partially absorbed yolk sac) was captured in a collection bottle on June 7 (day 51 post fertilization). Alevins of Lake Superior origin began emergence on June 13 (day 49-51 post fertilization). Emergence peaked during June 12-17 and on June 21 for alevins of Normandale and Lake Superior stock respectively (Figure 7). It should be noted that fertilization dates and temperature regimes were different for the two sets of eggs (see Table 2).

A total of 389 alevins (13.3% of original egg number) emerged from the limestone buffered Normandale eggs while only 4 (0.1%) emerged from Normandale eggs incubated in mixed gravel (Table 6). Limestone protected Lake Superior eggs exhibited even higher egg-alevin survival (n = 981; 61.0%)

again, a reflection of their sheltered position (i.e. not affected by water turbulence and associated pH reduction). Only one alevin (<0.1%) emerged from Lake Superior eggs incubated in mixed gravel.

When the experiment was terminated (June 28) an additional 10 live fry (yolk sacs absorbed) of Lake Superior origin were found in limestone filled hatching boxes (only dead eggs and fry recovered in all other boxes). Addition of these to the total increases the egg-alevin survival rate for limestone incubated Lake Superior eggs to 61.6%.

The intermediate sac fry-alevin survival rate can be calculated from the two determined survival rates (egg-sac fry; egg-alevin). On the south shore, the calculated survival of sac fry (Table 7) was much greater in limestone (23.2%) than in mixed gravel (0.7%) even though hatching success (egg-sac fry) was similar in the two substrates (57.4%, 57.1% - Table 5). It should be noted that during the yolk sac absorption period (~May 28-June 15) pH fluctuations within the limestone substrates were less extreme (i.e.: generally higher pH) than prior to hatching (Figure 5). Along the north shore, under optimal conditions (sheltered), sac fry survival was 70.9% in limestone and 0.4% in mixed gravel.

Although limestone clearly provided protection during hatching and yolk sac absorption, survival of the alevins upon return to ambient lake water was minimal (Table 8). Mortality of alevins hatched in limestone substrates was 65.2 to 78.8%

within 5 days of transfer to holding pens in George Lake. In contrast, no mortality occurred in the holding pen in Fairbank Lake (alevins hatched in Fairbank). Oxygen levels (∿100% saturation), water temperature (∿18°C) and feeding rates were similar in the two lakes.

Some degree of trace metal (particularly aluminum) toxicity on synergism with low pH may be implicated in the observed alevin mortality and the previously outlined hatching results. Schofield (1977) has reported toxic effects of aluminum on brook trout (Salvelinus fontinalis) at concentrations similar to those recorded in George Lake ($\bar{x}$ 250 ug/L). The present data base is much too scanty to adequately evaluate this aspect, however the limited information obtained suggests similar metal concentrations in the open lake and within hatching boxes, pointing to pH as the causative variable. Further evidence that changing pH (hatching area versus holding area) was the major factor affecting survival was obtained from holding experiments conducted in the Chikanishing River (Table 8). Mortality (5 day) was reduced from 65.2-78.8% in George Lake (pH ∿ 5.3) to 48.0% by moving alevins to a downstream (∿ 70 m) site with a pH of 5.6-5.9. At a further downstream site (∿ 1000 m) with a pH of 6.1-6.3 mortality was almost eliminated (2%). Metal concentrations at the downstream holding sites and in George Lake were similar, although metal speciation, and therefore potential for toxicity, may have been altered due to changing pH.

Only two alevins (from a total of 5 emerging) from the control (mixed gravel) boxes were captured for transfer to a holding pen in George Lake. No mortality occurred during the 5 day holding period.

DISCUSSION

The concept of utilizing limestone to protect trout eggs from acidic water is not new. Hatcheries have used limestone filters for this purpose as early as 1926 (Dahl, 1927). Small scale, *in situ* experimentation with limestone treatment is rare, however, particularly when the experimental design is restricted to protecting only incubating eggs and fry. The results of the present experiment clearly demonstrate that a relatively small application of limestone can greatly enhance the hatching success of eyed rainbow trout eggs in a lake of pH ∿ 5.3. In limestone filled hatching boxes, eyed-egg and sac fry survival rates were 86.9 and 70.9% respectively in contrast to the almost complete mortality observed among eggs and sac fry incubated in noncalcareous gravel.

Our results confirm previous observations that hatching and yolk sac absorption constitute a particularly pH sensitive developmental period for salmonids (Krishna, 1953; Schofield, 1965; EIFAC, 1969; Daye and Garside, 1977). In the first set of control (mixed gravel) hatching boxes ($\bar{x}$ pH - 5.4) survival rates decreased from 57.1% for eyed eggs to 0.2% for sac fry. In the second control set, mean egg and sac fry survival rates were 11.2 and 0.4% respectively. Obviously, the chorion and perivitelline fluid (see Knight, 1963) of the encapsulated embryo offer some protection from external acidic conditions; with hatching this protection is lost (Daye and Garside, 1977).

Although notable differences in parent stock existed between the two sets of eggs used in this experiment, the complicating factors of changing water temperatures and different chemical conditions (i.e.: acidic pulses along the exposed shoreline) make comparison of survival rates impossible. One can speculate on the significance of chemical similarities/differences between spawning and hatching waters (Phillips, 1959; Lloyd and Jordan, 1964; Schofield, 1965) as well as the genetic differences of wild versus domestic stock (Flick and Webster, 1976) however such hypotheses cannot be tested with the present data.

The fact that even a few alevins survived to emerge from the control boxes lends credence to the idea of selection for acid tolerant genetic strains (Gjedrem, 1976; Robinson et al, 1976). It should be noted that rainbow trout are probably the most acid sensitive salmonid species (Grande et al, 1978). In contrast to Kwain's (1975) results indicating that the mean lethal pH for rainbow trout embryos at 10°C was 4.75, Trojnar (1977) demonstrated that brook trout hatching success was 76% at pH 4.65 and Daye and Garside (1977) found that lower lethal pH limits for Atlantic salmon (Salmo salar) \embryos varied from 3.0-3.6 depending on developmental state. Grande et al (1978) attempted to rank the pH sensitivy of salmonid species using their own data and findings in the literature. They reported the following order of tolerance: rainbow trout, Atlantic salmon, brown trout (Salmo trutta) and brook trout, with the latter species the most resistant to low pH.

Our findings, while confirming the sensitivity of rainbow trout to low pH, indicate that *in situ* lethal limits are achieved at higher pH than suggested by laboratory studies. Lloyd and Jordan (1964) reported a laboratory 96 hr LC50 for yearling rainbow trout of pH 4.25 (hardness - 12 mg/L as $CaCO_3$; temperature - 14.5-17.5°C) and Kwain (1975) reported a median lethal pH of 4.75 for rainbow trout embryos (hardness - 20 mg/L as $CaCO_3$; temperature - 10°C); a 96 hr LC50 of 4.49 for fingerlings (hardness - 20 mg/L as $CaCO_3$; 10°C acclimation and 15°C test water temperatures); and a 96 hr LC50 of pH 3.38 for yearlings (hardness - 20 mg/L as $CaCO_3$; 10°C acclimation and test temperature). In our study, egg-alevin mortality exceeded 98% in the unbuffered control boxes although pH never dropped below 5.2, agreeing well with Berzin's (1960) findings that the lower tolerance limit for rainbow trout may be as high as pH 5.5-6.0 in natural waters.

The increased pH sensitivity of salmonids in natural aquatic systems appears to be a response to the influence of other environmental stresses. As suggested earlier, trace metals such as aluminum may have contributed to the observed mortality in George Lake. Further, the low degree of acid tolerance observed in our experiment may reflect the very dilute nature of the study lake, since the effects of low pH on fish populations seem most pronounced in waters of low ionic strength (Wright and Snekvik, 1978).

Although incubation in limestone protected rainbow trout eggs and fry on a sheltered shoreline, emergent alevins were unable to withstand the pH gradient between interstitial

water (x 6.6) and the lake proper (x̄ 5.3). Trojnar (1977) reported similar results with brook trout, however, hard water (conductivity - 231.8 umho's/cm) was used in that experiment and the pH changes (8.0-5.6,5.0,4.6 and 4.0) were much greater than existing in our in situ study. In contrast, Ozburn (1976) found that brook trout alevins (50 days post hatch) transferred from a control tank (pH 6.0 ± 0.2; conductivity - 57.5 umho's/cm) to test water with a pH of 5.5 suffered only 15% mortality during a 120 day holding period. Ozburn's (1976) data suggest that the alevin survival rate may have been much higher had eggs from a more acid tolerant species such as brook trout been used in the present study.

The low survival rate of emergent alevins of our test species (rainbow trout) casts doubt on the potential use of small scale limestone treatments, however, several practical applications are possible and should be tested. In lakes, or areas of lakes subject to short term, episodic (e.g. snow melt) depression of pH, limestone could protect incubating eggs and fry until water quality improves. The use of relatively acid resistant salmonid species or strains may greatly reduce past emergent mortality and enhance the effectiveness of limestone treatment. Limestone spawning beds could be constructed at creek mouths or spring upwellings to capitalize on the fact that some salmonid species prefer to spawn in alkaline waters (Johnson and Webster, 1977). If such applications are successful, incubation of eyed eggs within limestone substrates could prove an efficient and inexpensive alternative to the stacking of adults/yearlings/fry in attempts to maintain or restore salmonid populations in acidic lakes. Additionally, artificial limestone spawning beds could provide additional protection in conjunction with whole lake neutralization.

REFERENCE

ARCE, R. G. and C.E. BOYD, 1975. Effects of agricultural limestone on water chemistry, phytoplankton productivity and fish production in soft-water ponds. Trans. Am. Fish Soc. 2: 308-312.

BEAMISH, R. J., 1974. Loss of fish populations from unexploited remote lakes in Ontario, Canada as a consequence of atmospheric fallout of acid. Wat. Res. 8: 85-95.

BEAMISH, R. J., W. L. LOCKHART, J. C. VAN LOON and H. H. HARVEY, 1975. Long-term acidification of a lake and resulting effects on fishes. Ambio, 4: 98-102.

BERZINS, B., 1960. Kalkning av sjoar - Sodra Svoriges Fiskeriforening 1959-60: 28-35. In - Grande et al, 1978.

BOWLING, M.L. and R. L. BUSBEE, 1964. A three year study on the effects of lime applications on the standing crops of benthic organisms in Georgia farm ponds. Proc. S.E. Assn. Game and Fish Commissions, 18: 280-302.

CHAKOUMAKOS, C., R.C. RUSSO and R. U. Thurston, 1979. Toxicity of copper to cutthroat trout (salmo clarki); under different conditions of alkalinity, pH and hardness. Envir. Sci. Technol. 13(2): 213-219.

COLLINS, J. J., 1975. An emergent fry trap for lake spawning salmonines and coregonines. Prog. Fish. Cult. 37(3): 140-142.

CRAIG, G. R. and W. F. BAKSI, 1977. The effects of depressed pH on flagfish reproduction, growth and survival. Wat. Res. 11: 621-626.

DAHL, K., 1927. The effect of acid water on trout fry. Salmon Trout Mag. 46: 35-43.

DAYE, P. G. and E. T. GARSIDE, 1977. Lower lethal levels of pH for embryos and alevins of Atlantic salmon, Salmo salar L. Can. J. Zool. 55: 1504-1508.

EUROPEAN INLAND FISHERIES ADVISORY COMMISSION (EIFAC), 1969. Water quality criteria for European fresh-water fish. Report on extreme pH values and inland fisheries. Wat. Res. 3: 593-611.

FLICK, W.A. and D. A. WEBSTER, 1976. Production of wild, domestic, and interstrain hybrids of brook trout (Salvelinus fontinalis) in natural ponds. J. Fish. Res. Board Can. 33: 1525-1539.

GJEDREM, T., 1976. Genetic variation in tolerance of brown trout to acid water. SNSF - project, Aas, Norway, Research Rept. FR 5/76, 11 pp.

GRAHN, O. and H. HULTBERG, 1975. The neutralizing capacity of 12 different lime products used for pH-adjustment of acid water. Vatten, 2: 120-132.

GRANDE, M., I.P. MUNIZ, and S. ANDERSEN, 1978. Relative tolerance of some salmonids to acid waters. Limn. Oceanogr. 20: 2070-2084.

HARRISON, V.F., 1969. Neutralization and aeration of acid mine waters - a literature survey. Dept. of Energy, Mines and Resources, Ottawa, Canada, Information Circular 222.

HASLER, D. H., O. M. BRYNILDSON and W. T. HELM, 1951. Improving conditions for fish in brown-water bog lakes by alkalization. J. Wild. Mgmt. 15 (4): 347-352.

HODSON, P.V., B. R. BLUNT, and D. J. SPRY, 1978. pH - induced changes in blood lead of lead-exposed rainbow trout (salmo gairdneri) J. Fish. Res. Board Can. 35: 437-445.

HOOPER, W., 1979. Personal communication.

HULTBERG, H. and O. GRAHN, 1975. Some effects of adding lime to lakes in Western Sweden. Unpublished manuscript, 15 pp.

JEFFRIES, D. S., C. M. COX and P. J. DILLON, 1976. The depression of pH in lakes and streams in central Ontario during snowmelt. M.O.E. Tech. Rept. 23 pp.

JENSEN, R. W. and E. SNEKVIK, 1972. Low pH levels wipe out salmon and trout populations in southermost Norway. Ambio, 1(6): 223-224.

JOHANSSON, N., J. E. KIHLSTROM and A. WAHLBERG, 1973. Low pH values shown to affect developing fish eggs (Brachydanio rerio Ham-Buch). Ambio, 2: 42-43.

JOHNSON, D. W. and D. A. WEBSTER, 1977. Avoidance of low pH in selection of spawning sites by brook trout (Salvelinus fontinalis). J. Fish. Res. Board Can. 34: 2215-2218.

KENNEDY, L.A., 1979. Teratogenesis in lake trout (Salvelinus namaycush) in a whole lake acidification experiment - unpub. manuscript.

KNIGHT, A.F., 1963. The embryonic and larval development of the rainbow trout. Tran. Ass. Fish. Soc., 94(4): 344-355.

KRISHNA, D., 1953. Effects of changing pH on developing trout eggs and larvae. Nature (London) 171: 434.

KWAIN, W., 1975. Effect of temperature on development and survival of rainbow trout, Salmo gairdnerii in acid waters. J. Fish. Res. Board Can. 32: 493-497.

LLOYD, R. and D. H. M. JORDAN, 1964. Some factors affecting the resistance of rainbow trout (Salmo gairdnerii Richardson) to acid waters. Int. J. Air. Wat. Poll. 8: 393-403.

MENENDEZ, R., 1976. Chronic effects of reduced pH on brook trout (Salvelinus fontinalis). J. Fish. Res. Board Can. 33: 118-123.

MNR (MINISTRY OF NATURAL RESOURCES, ONTARIO), 1979. Unpublished lake survey data.

MOUNT, D.I., 1973. Chronic effect of low pH on fathead minnow survival, growth and reproduction. Water Res. 7: 987-993.

NEESS, J. C., 1949. Development and status of pond fertilization in Central Europe. Trans. Am. Fish. Soc. 76: 335-358.

OZBURN, G. W., 1976. Unpublished data.

PHILLIPS, A. M. Jr., 1959. The known and possible role of minerals in trout nutrition and physiology. Trans. Am. Fish. Soc. 88: 133-135.

ROBINSON, G. D., DUNSON, W.A., WRIGHT, J. E. and G. E. MAMOLITO, 1976. Differences in low pH tolerance among strains of brook trout (Salvelinus fontinalis). J. Fish. Biol. 8: 5-17.

RUBY, S.M., J. ACZEL and G. R. CRAIG, 1978. The effects of depressed pH on spermatogenesis in flagfish Jordanella floridae. Wat. Res. 12: 621-626.

SCHEIDER, W. A., J. ADAMSKI and T. M. PAYLOR, 1975. Reclamation of acidified lakes near Sudbury, Ontario, MOE Tech. Rep. 129 pp.

SCHOFIELD, C. L. Jr., 1965. Water quality in relation to survival of brook trout, Salvelinus fontinalis (Mitchill) Trans. Am. Fish. Soc. 94: 227-236.

SCHOFIELD, C. L. Jr., 1976. Acid precipitation effects on fish. Ambio 5(5-6): 228-230.

SCHOFIELD, C. L. Jr., 1977. Acid snow-melt effects on water quality and fish survival in the Adirondack Mountains of New York State. Res. Proj. Tech. Compl. Rept. Project No. A-072 - NY.

TROJAR, J. R., 1977. Egg hatchability and tolerance of brook trout fly (Salvelinus fontinalis) under low pH conditions. J. Fish. Res. Board Can. 34: 474-479.

WATERS, T. F., 1956. The effects of lime application to acid bog lakes in northern Michigan. Trans. Am. Fish. Soc. 86: 329-344.

WATERS, T. F. and R. C. BALL. Lime application to a soft-water, unproductive lake in northern Michigan. J. Wildl. Mgmt. 21 (4): 385-391.

WRIGHT, R. F. and E. SNEKVIK, 1978. Acid precipitation: chemistry and fish populations in 700 lakes in southern most Norway. Verh. Internat. Verein. Limnol. 20: 765-775.

YAN, N. D., W. A. SCHEIDER and P. J. DILLON, 1977. Chemical and biological changes in Nelson Lake, Ontario, following experimental elevation of lake pH. Pros. Wat. Poll. Res. Can. 12: 213-231.

TABLE 1. Comparative summary of water chemistry, George and Fairbank lakes (based on sampling conducted May 15-June 28 in George Lake and May 16-June 21 on Fairbank Lake)

	George Lake			Fairbank Lake		
	$\bar{x}$	Range	n	$\bar{x}$	Range	n
pH	5.33	5.19-5.59	13	7.09	6.70-7.40	6
Conductivity umho's/cm	37	36-39	13	65	65-66	6
T.F.E. alkalinity mg/L as $CaCO_3$	5	3-7	13	14	12-15	6
Calcium mg/L	3.0	2.8-3.2	13	7.3	7.2-7.4	6
Magnesium mg/L	0.76	0.70-0.95	12	1.53	1.50-1.55	6
Sodium mg/L	0.80	0.60-1.00	13	1.02	0.90-1.10	6
Potassium mg/L	0.46	0.35-0.60	13	0.51	0.40-0.55	6
Sulphate mg/L	11.9	11.5-13.0	13	15.1	15.0-15.5	6
Chloride mg/L	0.60	0.50-0.90	13	0.61	0.55-0.70	6
Nitrate mg/L	0.149	0.139-0.183	13	0.058	0.009-0.254	6
Copper ug/L	6	<1-11	13	6	3-9	4
Nickel ug/L	9	7-20	12	<3	<2-<4	5
Zinc ug/L	26	17-36	13	4	<2-8	4
Aluminum ug/L	250	150-560	13	41	10-90	6
Manganese ug/L	150	140-170	11	11.5	8-20	6
Iron ug/L	148	40-610	13	46	<10-140	6

TABLE 2. Background data on rainbow trout eggs used in hatching experiments.

	Normandale eggs	Lake Superior eggs
Hatchery location (Lat/Long)	Normandale ($42^{o}43'/80^{o}19'$)	Sault Ste. Marie ($46^{o}31'/84^{o}20'$)
Source of parent stock	domestic-Normandale brood stock	wild-Lake Superior
Age of parent stock	3-6 years	3-6 years
Fertilization date	April 17/79	April 23-25/79
Incubation temperature (^{o}C)	9	7
total Hardness (mg/L $CaCO_3$)	194	38
pH	7.8 - 8.0	6.95
Planting date	May 10/79	May 24/79
Egg size (volume;ml;$\bar{x}\pm SD$)	0.076 ± 0.002	0.099 ± 0.002[a] 0.091 ± 0.004 0.064 ± 0.003
Mortality rate in hatchery	<2.0%[b]	0.3%[c]

[a] three separate egg batches used

[b] Hooper (1979)

[c] Determined from batch of 981 eggs left in hatchery

TABLE 3. Comparative summary of selected chemical parameters within substrates and in ambient George and Fairbank lakes

	Location							
	George - South Side			George - North Side			Fairbank	
	NL-1 (limestone)	NG-1 (mixed gravel)	Lake	SL-1 (limestone)	SG-1 (mixed gravel)	Lake	F-1 (mixed gravel)	Lake
pH								
min.	5.60	5.22	5.19	6.23	5.39	5.30	6.70	6.70
max.	8.50	6.05	5.59	7.63	5.95	5.50	7.42	7.40
$\bar{x}$	6.25	5.44	5.33	6.58	5.57	5.38	7.06	7.09
S.D.	0.69	0.23	0.13	0.44	0.17	0.07	0.28	0.31
n	(13)	(13)	(13)	(9)	(9)	(9)	(6)	(6)
Conductivity								
min.	36	36	36	38	36	36	65	65
max.	64	44	39	57	39	38	67	66
$\bar{x}$	44	38	37	45	37	36	66	65
S.D.	9	2	1	6	1	1	1	1
n	(12)	(12)	(12)	(9)	(9)	(9)	(6)	(6)
Alkalinity								
min.	3	3	3	5	3	3	12	12
max.	22	6	7	14	7	5	15	15
$\bar{x}$	8	5	5	9	5	4	14	14
S.D.	6	1	1	3	1	1	1	1
n	(12)	(12)	(12)	(9)	(9)	(9)	(6)	(6)
Calcium								
min.	3.0	2.8	2.8	3.6	2.6	2.8	7.2	7.2
max.	9.0	4.6	3.2	7.2	3.2	3.2	7.8	7.4
$\bar{x}$	4.5	3.1	3.0	4.9	3.0	3.0	7.4	7.3
S.D.	2.0	0.5	0.2	1.2	0.2	0.1	0.2	0.1
n	(12)	(12)	(12)	(9)	(9)	(9)	(6)	(6)

TABLE 4. Comparison of waterborne trace metal concentrations within a crushed limestone substrate and in ambient George Lake water (July 11 and July 20, 1979)

Sample	Date	Total metal concentration (ug/L)					
		Cu	Ni	Zn	Fe	Mn	Al
Interstitial water within limestone substrate (NL-1)	July 11	1	9	22	140	89	210
	July 20	1	8	30	40	150	150
Ambient lakewater	July 11	4	11	28	98	120	200
	July 20	1	5	30	60	80	190

TABLE 5. Hatching success (egg-sac fry) of rainbow trout eggs placed in artificial substrates in George and Fairbank lakes[a]

Hatching substrate	Box	Original egg number	Number of dead eggs	Hatching success (%)
George Lake (pH 5.2-5.6): Normandale stock				
Limestone (experimental, pH 5.6 - 8.5)	NL-1	644	248	61.5
	NL-2	966	410	57.6
	NL-3	966	453	53.1
				$\bar{x}$ 57.4
Mixed gravel (control, pH 5.2 - 6.1)	NG-1	644	244	62.2
	NG-2	966	421	56.4
	NG-3	966	456	52.8
				$\bar{x}$ 57.1
Lake Superior stock[c]				
Limestone (experimental, pH 6.2 - 7.6)	SL-1	327	70	78.6
	SL-2	538	36	93.3
				$\bar{x}$ 86.9
Mixed gravel (control, pH 5.4 - 6.0)	SG-1	327[d]	336	00.0
	SG-2	538	418	22.3
				$\bar{x}$ 11.2
Fairbank Lake (pH 6.7 - 7.4): Normandale stock				
Mixed gravel	N-1	644	36	94.5
	N-2	966	94	90.3
	N-3	966	36	96.3
				$\bar{x}$ 93.7
Lake Superior stock				
Mixed gravel	S-1	775	16	97.9

[a] Hatching success determined from count of dead eggs in Whitlock Vibert Boxes (WVB) two weeks after eyed-eggs were placed in them.

[b] Site subject to wind driven acid pulses.

[c] Sheltered site; interstitial water in limestone remained at elevated pH (6.2 - 7.6); pH in control boxes (mixed gravel) = 5.4 - 6.0

[d] Determined volumetrically; $\bar{x}$ = 327, 95% conf. limits 308-345

TABLE 6. Survival (egg-alevin) of rainbow trout eggs planted in artificial substrates in George Lake[a]

Hatching substrate	Box	Original egg number	Number of emergent alevins	Survival rate (egg-alevin) (%)
Normandale stock[b]				
Limestone (experimental, pH 5.6 - 8.5)	NL-4	966	166	17.2
	NL-5	966	177	18.3
	NL-6	966	46	4.8
				$\bar{x}$13.3
Mixed gravel (control, pH 5.2 - 6.1)	NG-4	966	0	00.0
	NG-5	966	4	00.4
	NG-6	966	0	00.0
				$\bar{x}$00.1
Lake Superior stock[c]				
Limestone (experimental, pH 6.2 - 7.6)	SL-3	775	450	58.1
	SL-4	775	495	63.9
				$\bar{x}$61.0
Mixed gravel (control, pH 5.4 - 6.0)	SG-3	775	1	00.1
	SG-4	775	0	00.0
				$\bar{x}$ <.1

[a] emergent traps above hatching boxes collected the swimming alevins; emergence began on June 5; collections continued until June 28.

[b] Site subject to wind driven acid pulses.

[c] Sheltered site; interstitial water in limestone filled boxes remained at pH 6.2 - 7.6; pH in control boxes (mixed gravel) = 5.4 - 6.0.

TABLE 7. Survival (sac fry - alevin) of rainbow trout eggs planted in artificial substrates in George Lake

Hatching substrate	Egg - sac fry survival rate %	Egg - alevin survival rate %	sac fry - alevin[a] survival rate %
Normandale stock			
Limestone	57.4	13.3	23.2
Mixed gravel	57.1	0.1	0.2
Lake Superior stock			
Limestone	86.9	61.6[b]	70.9
Mixed gravel	11.2	0.05	0.4

[a] Calculated from the two determined survival rates (eggs - sac fry; egg - alevin).

[b] Includes 10 live alevins found in limestone filled boxes when experiment was terminated on June 28.

(give pictorial view of stages in Trt /

TABLE 8. Mortality rate of rainbow trout alevins after leaving hatching boxes

Hatching Substrate (pH)	Holding site (pH)	Original number Day 0	Dead alevins (cumulative total) Day 1	Day 2	Day 3	Day 4	Day 5	Mortality (%)
George Lake (experimental site):								
Limestone (6.2-7.6)	Ambient lake 1 (5.2-5.6)	23	3	10	12	13	15	65.2
	11	52	11	34	40	41	41	78.8
	Outlet stream[b] (5.6-5.9)	50	10	19	21	22	24	48.0
	Outlet stream[c] (6.1 - 6.3)	50	0	0	0	0	1	2.0
Mixed gravel (5.4-6.0)	Ambient lake (5.2-5.6)	2[d]	0	0	0	0	0	00.0
Fairbank Lake								
Mixed gravel (6.7-7.4)	Ambient lake (6.7-7.4)	50	0	0	0	0	0	00.0

[a] Transferred from collection bottles to screen covered holding boxes (0.6 x 0.6 x 0.3 m); held for 5 days; fed formulated trout diet daily.

[b] Site located ∿ 70 m downstream from the experimental installation at the outlet of George Lake.

[c] Site Located ∿ 1000 m downstream from the experimental installation at the outlet of George Lake; buffering provided by clay deposits and inflowing springs.

[d] Only 5 fish survived to swim up from the gravel filled boxes, 2 died and 1 escaped before transfer to holding box.

FIGURES

FIGURE 1: General locations of the study lakes with reference to Sudbury.

FIGURE 2: Hatching boxes used for incubation of eyed rainbow trout eggs. On the left is an empty uncovered box fitted with a sampling tube; on the right a hatching box with an attached emergent trap.

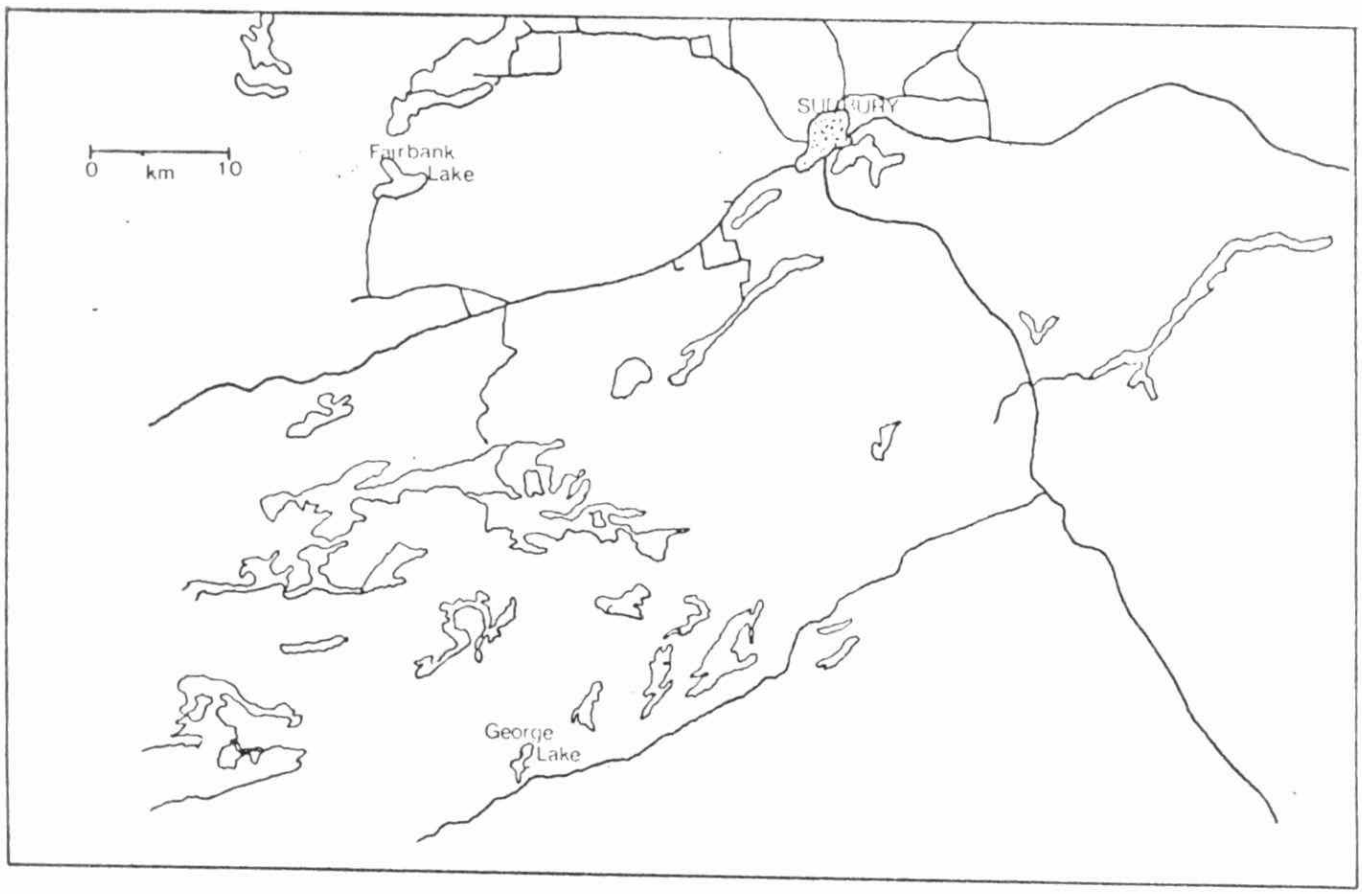
FIGURE 3: The experimental installation, George Lake. SL= Lake Superior stock, limestone substrate; SG= Lake Superior stock, mixed gravel substrate; NL= Normandale stock, limestone substrate; NO= Normandale stock, mixed gravel substrate.

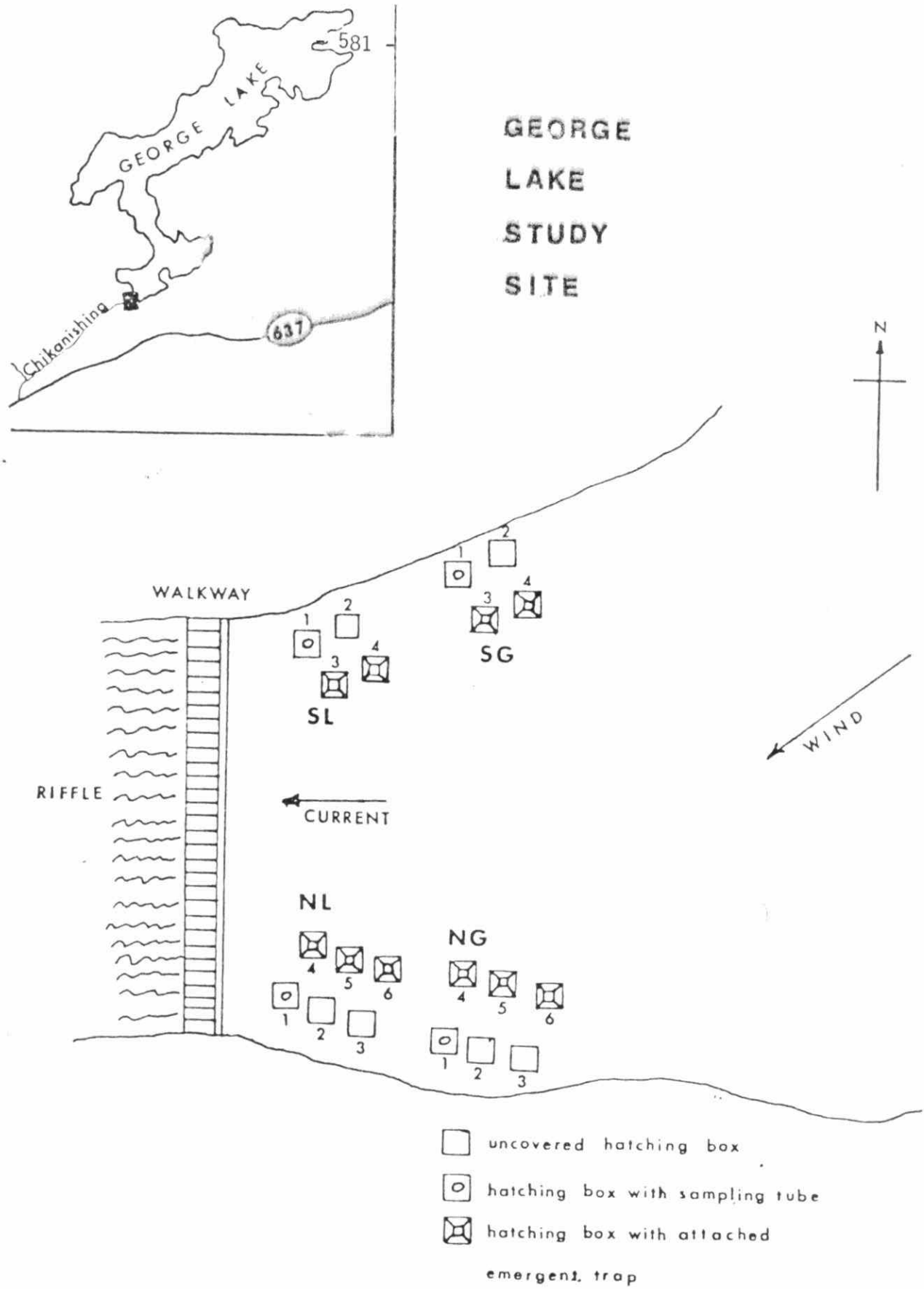
FIGURE 4: The experimental installation, Fairbank Lake. S= Lake Superior stock; N= Normandale stock (mixed gravel substrate only).

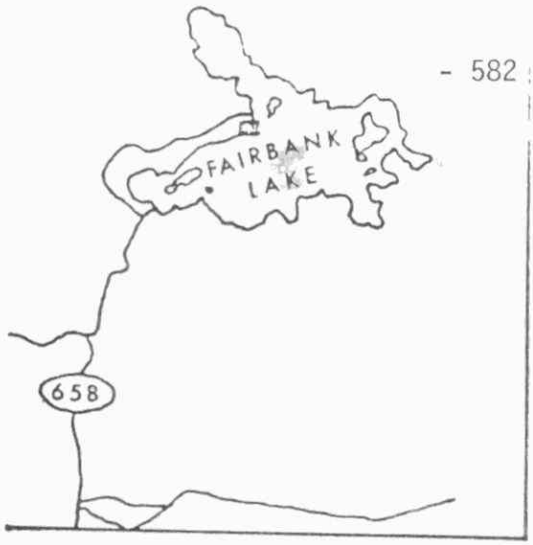
FIGURE 5: Temporal pH variation within substrates and in ambient lake water, on the south shore of the George Lake outlet.

FIGURE 6: Temporal pH variation within substrates and in ambient lake water, on the north shore of the George Lake outlet.

FIGURE 7: Chronology of alevin emergence, George Lake.


0 km 10
Fairbank Lake
SUDBURY
George Lake


581
GEORGE LAKE
Chikanishing
637
GEORGE
LAKE
STUDY
SITE
N
WALKWAY
SG
SL
WIND
RIFFLE
CURRENT
NL
NG
uncovered hatching box
hatching box with sampling tube
hatching box with attached
emergent trap



FAIRBANK

LAKE

STUDY

SITE

N

WIND

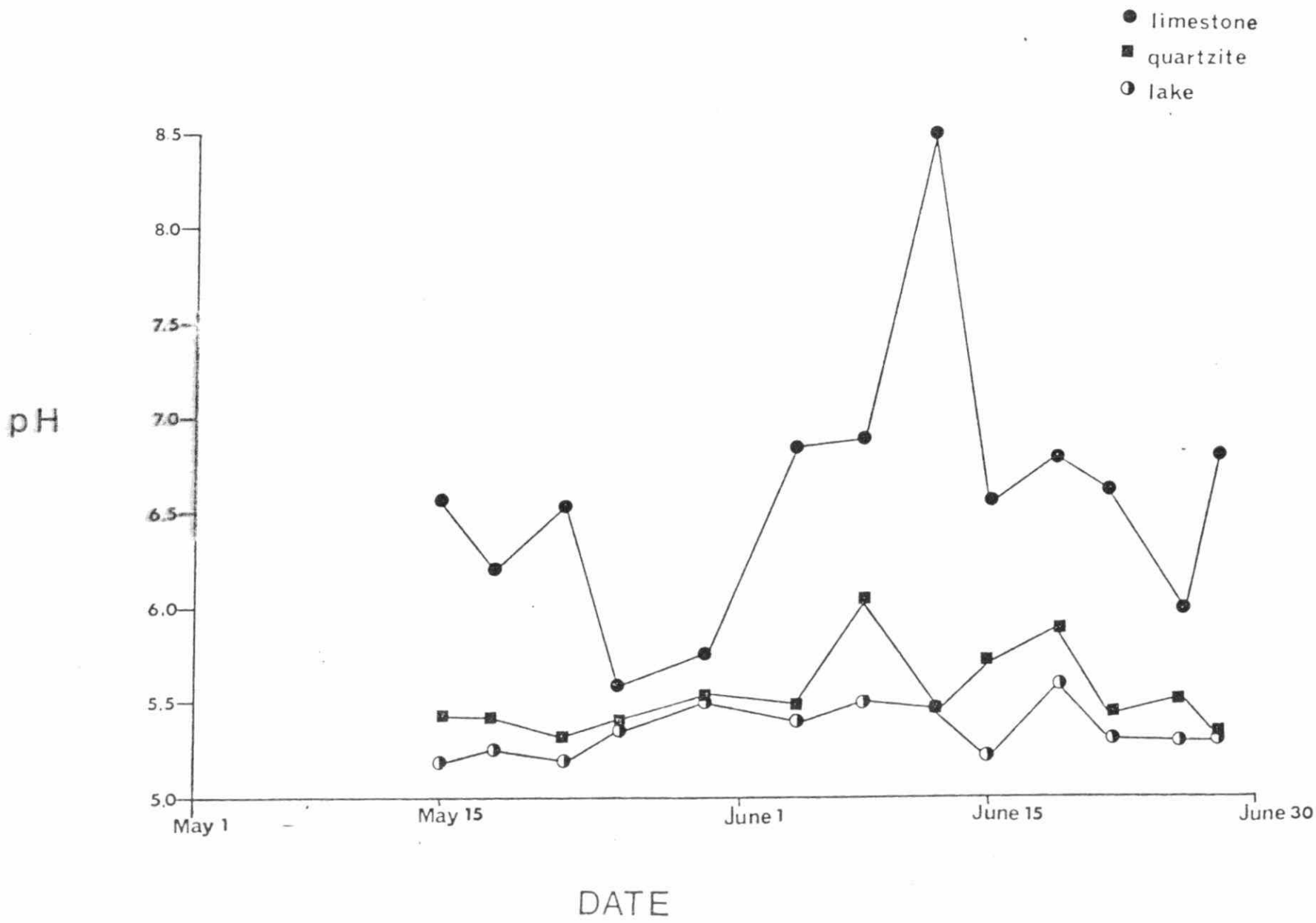
S
1

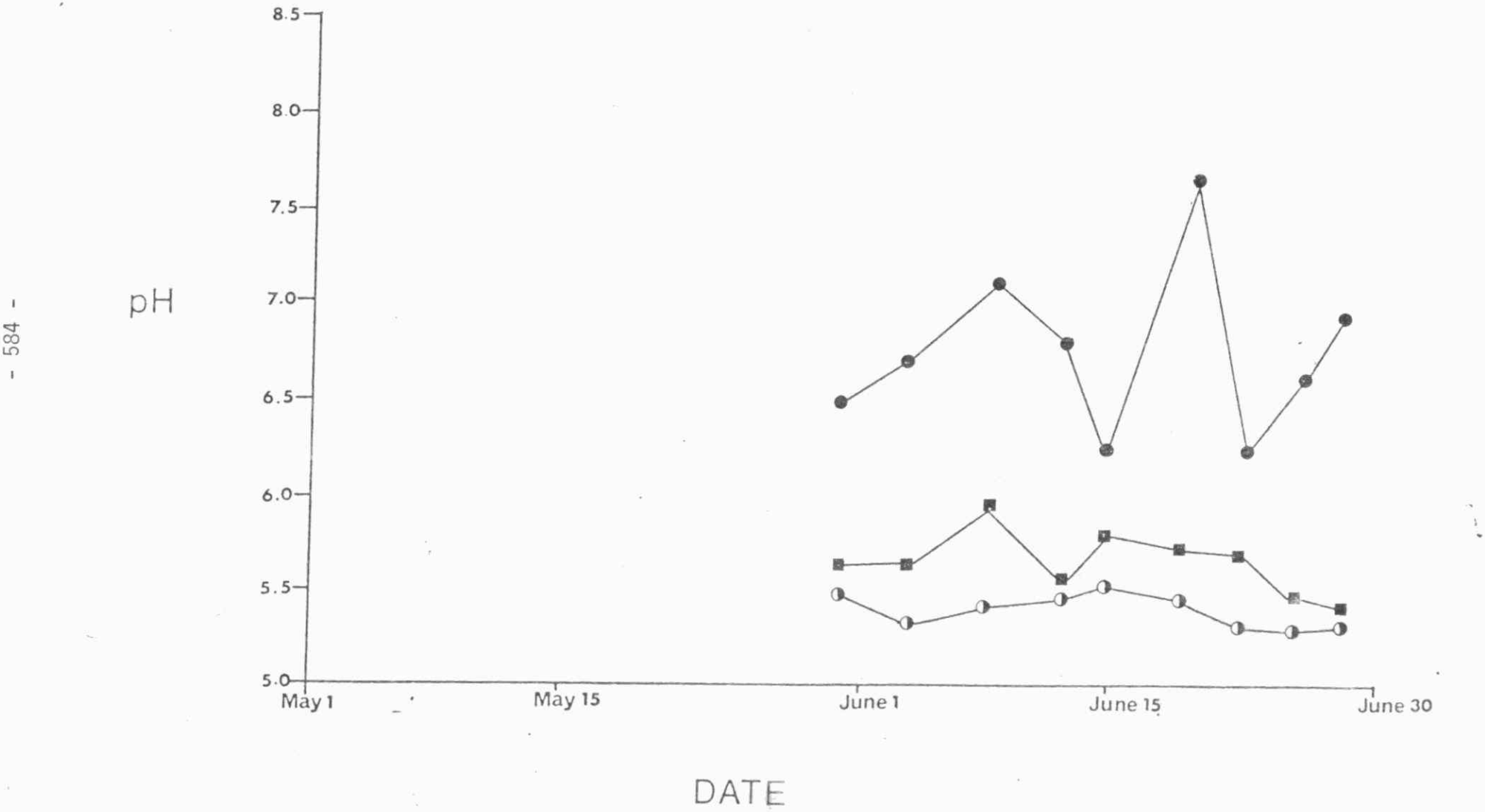
N
1
2
3

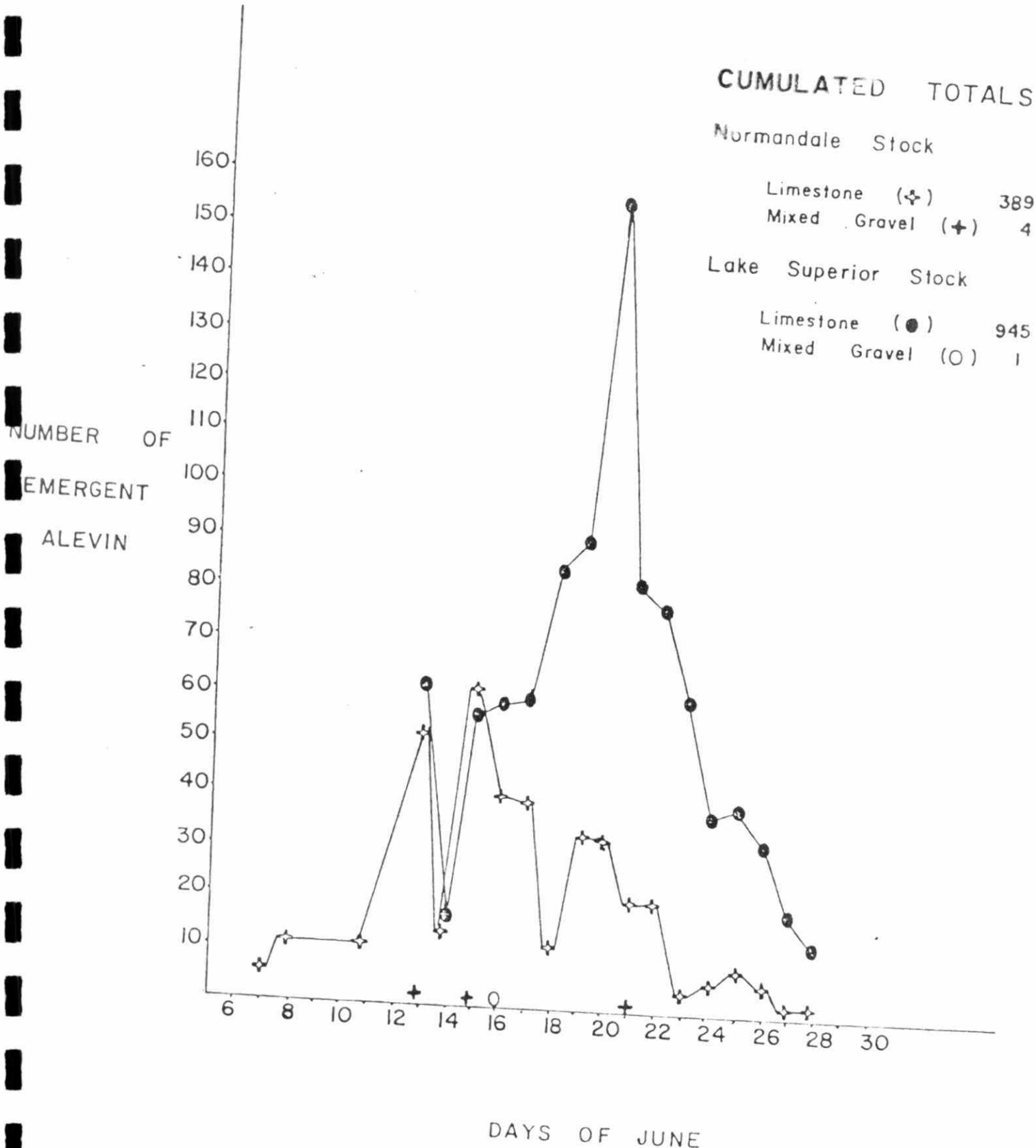
uncovered hatching box

hatching box with sampling tube

BOAT
DOCK


limestone
quartzite
lake
pH
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
May 1
May 15
June 1
June 15
June 30
DATE


limestone
quartzite
lake
pH
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
May 1
May 15
June 1
June 15
June 30
DATE


CUMULATED TOTALS
Normandale Stock
Limestone (✧) 389
Mixed Gravel (+) 4
Lake Superior Stock
Limestone (●) 945
Mixed Gravel (O) 1
NUMBER OF EMERGENT ALEVIN
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
6
8
10
12
14
16
18
20
22
24
26
28
30
DAYS OF JUNE

APPENDIX TWENTY-FOUR

MNR 1980/81 LRTAP PROGRAM

The Ministry of Natural Resources program in 1980/81 is not completely firm as yet, partly because of uncertainties with funding, and partly because in several instances plans are still evolving. However, there are a number of areas in which we do expect to make a contribution.

I. Monitoring

1. We intend to increase our monitoring of lakes to assess susceptibility to acidification (Task #1 of A.P.I.O.S.). This year nine crews participated, sampling in excess of 250 lakes. We expect to probably double that next year which will substantially increase the data base. The areas we will do have not yet been determined, but when all the data are available we will meet with MOE to assess where we should be going from here.

2. We hope to monitor some streams next spring through the efforts of Algonquin Region and Parry Sound District. Seven tributaries to Georgian Bay which support walleye spawning runs will be sampled.

   In recent years there has been very poor recruitment of walleye to both the sport and commercial fishery of Georgian Bay. Previously this has been attributed to other stresses, e.g., overfishing. However, acidity during spring melt may be a major factor. Hence we hope to monitor pH in the spring at the time of spawning on the following rivers:

   Magnetwan
   Key
   French
   Shawanaga
   Seguin
   Moon
   Go Home

II. Process Studies

1. Frank Hicks of the Algonquin Fisheries Assessment Unit and Jim McLean of Fisheries Research will be continuing their work in Algonquin Park. This involves monitoring water chemistry and trying to assess pH effects on lake trout recruitment. There will also be some work on population estimates of lake trout, and continued creel census - the kind of work that over time will indicate what's happening to fish populations in response to various stresses (acidification being one).

2. Tony Kwain of Fisheries Research will be doing toxicity studies on various species of fish including lake trout, smallmouth bass and walleye, basically trying to identify the most pH-sensitive life stages in these species.

   The objective is to determine just how recruitment is affected by pH in these species.

   Kwain will also be involved in the Algoma studies collecting fisheries information on the Turkey L. System, in co-operation with John Kelso of DFO (species composition recruitment, etc.).

3. John Casselman will be pursuing his interest in the use of calcified tissue as an indicator of environmental stress. He intends to look at growth rates of scales and body in relation to pH to see just how growth rates can be used as an index of stress.

   In co-operation with Harold Harvey, Casselman will also be investigating heavy metal deposition and Ca metabolism in fish at different levels of pH. He is presently using a microprobe but later will use ion probe analysis. The ion probe is a new tool being acquired by University of Toronto which will provide very precise measurements of the elemental composition of various tissues.

III. Reclamation Studies

1. John Gunn will be continuing his efforts to investigate the feasibility of small-scale liming applications. He intends to use brook trout rather than rainbow trout used in the past. Gunn will again employ limestone to see if hatching success can be improved and to see if the species can be protected through its most sensitive stages before it is exposed to acidic conditions.

2. A lake reclamation is also tentatively planned for this winter, in co-operation with Northeastern Region, MOE. The lake involved is Hamilton L. in the Chapleau area. This is a former brook trout lake that is now very acidic (pH $\sim$ 4.6). The plan is to neutralize the lake with limestone on an experimental basis, with the hope of eventually stocking brook trout or perhaps Aurora trout.

IV. Socio-economic Studies

We will be participating with Fisheries & Oceans in a provincial angler survey in 1980-81. Because we do not have a resident angling licence, we will have to use a household survey of persons selected from voters lists.

We think this survey can be designed so as to provide information that will be helpful in assessing socio-economic effects of acid rain.

At the very least, it will give us good data on where people are fishing, how much they spend, number of angler days, etc.

If the proper questions are asked, we can also determine whether people would continue to fish if large numbers of lakes were lost to acidification, and if so, where they would go. This would also help to indicate where higher fishing pressure can be expected in the future.

We think this is very important information to have and it is just not available at the moment from other sources.

The results of the survey should be available some time in 1981.

In terms of a general direction for the Ministry, we expect to become more heavily involved in assessing the impact of acidification on fish populations. This type of study will be done by both existing and new fisheries assessment units, which are charged with providing long-term data on the status of fish populations and on their response to stress.

A number of new assessment units are going to be established in the future, at a rate depending on funding. New units in acid-sensitive areas have been given top priority, specifically units for the Algoma and Haliburton areas. However, at the moment it is uncertain as to just when these units can be established.

J. T. Allin
Fisheries Branch
Ontario Ministry of Natural Resources

September 27, 1979

Ontario

Ministry
of the
Environment

135 St. Clair Avenue W
Suite 100
Toronto, Ontario
M4V 1P5

RECEIVED
JUN -2 1980
PROGRAM PLANNING

1980 05 30

M E M O R A N D U M

TO: Messrs. B. Drowley,
D. Jeffs,
T. Cross,
G. Ronan,
C. E. McIntyre,
A. Castel,
R. Gotts,
B. Steggles.

FROM: J. C. Mittermayer,
Assistant to the Coordinator,
A.P.I.O.S.

RE: Acidic Precipitation Seminar at
Killarney, Ontario.

Enclosed please find a Summary of the Proceedings of the Ontario-Canada Research Coordination Group LRTAP - Acidic Precipitation Seminar at Killarney, Ontario, September 24-27, 1979.

To date the distribution list has been limited to conference attendees.

As you will note, the proceedings have been published in final form. However, if any participants wish to make changes, a compilation of amendments will be circulated for incorporation in the proceedings.

In addition, if you have any comments on any aspect of these minutes, please do not hesitate to contact me.

J. Mittermayer

J. C. Mittermayer.

JCM:bd

Encl.

QH
541.2
.S86
1979